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## Hydrogen spillover in the Fischer–Tropsch synthesis: An analysis of gold as a promoter for cobalt–alumina catalysts

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### ABSTRACT

This study investigated the operation of gold as a potential substitute for the platinum promoter in the Co/Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst. Au–Co/Al<sub>2</sub>O<sub>3</sub> was tested in conjunction with a model Hybrid Au–Co sample (comprised of a mechanical mixture of Au/Al<sub>2</sub>O<sub>3</sub> + Co/Al<sub>2</sub>O<sub>3</sub>) to investigate hydrogen spillover which has been demonstrated to play a vital role in the reduction promotion mechanism. TPR, TGA and in situ XRD provided evidence to support the improved reducibility of supported cobalt oxide crystallites in Au–Co/Al<sub>2</sub>O<sub>3</sub>. However, no improvement in the reducibility of the Hybrid Au–Co catalyst was observed, in contrast to previous studies on noble metal reduction promoters. It was hypothesized that even though gold-to-cobalt spillover occurred during reduction in Au–Co/Al<sub>2</sub>O<sub>3</sub>, the great separation between the gold and cobalt crystallites, combined with gold's much lower affinity for hydrogen activation adversely affected the efficiency of the spillover process in the hybrid sample. Nevertheless, Au–Co/Al<sub>2</sub>O<sub>3</sub> had an improved mass-based activity, and a turnover frequency comparable to a platinum promoted sample, which highlighted the potential of gold as a reduction promoter for Co/Al<sub>2</sub>O<sub>3</sub> catalysts.

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### 1. Introduction

The commercial Co/Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst comprises small nano-sized cobalt crystallites that maximise the active surface area during the reaction. However, small cobalt crystallites are susceptible to strong metal support interactions (SMSIs) with the alumina support, which hinders their reduction and results in the need for reduction promoters [1–13]. Small quantities of noble metals such as platinum, rhenium, ruthenium, rhodium, and palladium have been observed to significantly improve the reducibility of cobalt-based catalysts to the desired metallic active phase during catalyst activation [1–13]. The use of platinum as the promoter of choice in commercial catalysts is favoured by its global availability and production, which far exceed those of other noble metals. A recent study that used a Hybrid Pt–Co catalyst (mechanical mixture of 20 wt.-% Co/Al<sub>2</sub>O<sub>3</sub> + 0.5 wt.-% Pt/Al<sub>2</sub>O<sub>3</sub>) to investigate the functioning of platinum as a reduction promoter provided evidence in support of a

spillover mechanism [14]. The extent of reduction of the hybrid Pt–Co catalyst was greatly improved compared to an unpromoted Co/Al<sub>2</sub>O<sub>3</sub> sample, which implied that direct promoter–cobalt contact was not required to facilitate the reduction of cobalt oxide. It was proposed that the reduction involved a hydrogen spillover mechanism that was initiated by dissociative hydrogen adsorption on the noble metal promoter surface, followed by surface migration of the hydrogen species to the cobalt oxides for reaction.

Besides noble metals, Group 11 'coinage' metals such as copper, silver and gold have also been observed to improve the reducibility of cobalt-based catalysts [15–18]. Until the mid-1980s, the study of gold as a catalyst was all but abandoned because of its strong noble character, which rendered it unreactive and irrelevant for catalytic chemistry. The turning point in gold catalysis came in the form of the discoveries made by Hutchings [19,20] and by the group of Haruta [20,21] who demonstrated that supported nano-sized gold crystallites were active for acetylene hydrochlorination and low temperature oxidation of H<sub>2</sub> and CO, respectively. Since then, the wealth of literature and knowledge of gold catalysis has continued to grow especially for oxidation reactions.

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Unfortunately, the strong focus on the use of gold as an oxidation catalyst has skewed the attention away from its use in other reactions such as hydrogenation for which it has exhibited appreciable catalytic activity [22]. With respect to hydrogenation, the binding energy of hydrogen atoms on gold surfaces and particularly Au(111) is lower than on Pt(111) [25]. Furthermore, hydrogen adsorption on gold is limited to low co-ordinated atoms along edges and at corners, which means that only a fraction of the surface of a gold crystallite may interact with hydrogen [23]. Nevertheless, gold has shown activity for carbon monoxide and carbon dioxide hydrogenation to methanol [20,24] and for selective hydrogenation of unsaturated compounds [25,26]. The interaction of hydrogen with only low coordination sites on gold implies that hydrogen activation on gold will be particle size dependent as reported during H/D exchange over Au/Al<sub>2</sub>O<sub>3</sub> [23,27].

The literature on gold under Fischer–Tropsch conditions (as a catalytic active material and/or as a promoter) is comparatively limited and in some cases contradictory compared to that on platinum and other noble metal promoters. Jacobs et al. [15], carried out a comprehensive study of Group 11 metals as promoters, which included samples of gold containing 0.1–5.05 wt.-% Au on 15 wt.-% Co/Al<sub>2</sub>O<sub>3</sub>. Gold was observed to improve the reducibility and activity of cobalt, but the C<sub>5</sub>+ selectivity started to decrease at gold loadings greater than 2 wt.-% (220 °C, 20 bar, H<sub>2</sub>/CO = 2). Ahmad et al. [28], using 1.5–2.5 wt.-% Au on 10 wt.-% Co/Al<sub>2</sub>O<sub>3</sub> also reported improvement in the cobalt reducibility. However, in contrast to Jacobs et al. [16], Ahmad et al. [30], found that the C<sub>5</sub>+ selectivities were higher than obtained with the unpromoted sample even at the highest gold loadings (220–275 °C, 1–5 bar, H<sub>2</sub>/CO = 2).

Jalama et al. [16], also investigated gold as a cobalt promoter and observed that the addition of 0.5–5 wt.-% Au improved the reducibility of 10 wt.-% Co on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> supported catalysts. However, an increase in the CH<sub>4</sub> selectivity was observed with a concomitant decrease in the C<sub>5</sub>+ selectivity even at the lowest Au loadings (220 °C, 20 bar, H<sub>2</sub>/CO = 2). Furthermore, a reduced olefin/paraffin ratio was observed, which implied an enhanced rate of (secondary) hydrogenation. In contrast, a separate study by the same group where 10 wt.-% Co on TiO<sub>2</sub> was promoted with 0.2–5 wt.-% gold [17] showed a decrease in the reducibility of supported cobalt oxides, although fewer cobalt titanate species were observed, which was attributed to the possible deposition of a gold layer between the cobalt crystallites and the titania support. The addition of gold up to a loading of 1 wt.-% increased the mass-based Fischer–Tropsch activity, which was ascribed to the presence of fewer cobalt–titanate species, but a further increase in the gold loading was detrimental to both the activity and C<sub>5</sub>+ selectivity.

Consequently, the objective of this study was to contribute to the rather limited body of literature on gold as a reduction promoter for the cobalt-based Fischer–Tropsch catalyst and to evaluate a possible substitution of the platinum promoter with gold. Gold is an attractive alternative because it is more abundant than platinum (annual global platinum production is only about 10% that of gold despite comparable spot prices per ounce). Furthermore, there is a great drive to find viable beneficiation outlets for gold in resource-rich countries such as South Africa. A key focus of the study was the investigation of hydrogen spillover as a mechanism by which gold promotes the reduction of supported cobalt oxides, via the use of a hybrid Au–Co catalyst sample. The hybrid Au–Co sample was a mechanical mixture of Au/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub>, which eliminated direct Au–Co contact and thus enabled the investigation of hydrogen spillover as a remote-control mechanism. It was hypothesized that the differences between the platinum versus gold reactivity towards H<sub>2</sub> and CO could provide key insights into the role of spillover hydrogen during cobalt reduction and during the Fischer–Tropsch synthesis.

## 2. Experimental

### 2.1. Catalyst preparation

A two-step slurry impregnation technique was used to prepare a 20 wt.-% Co/Al<sub>2</sub>O<sub>3</sub> sample using an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as the cobalt precursor [14]. Sasol Puralox SCCa 5-150, which was used as the γ-Al<sub>2</sub>O<sub>3</sub> support, was ground in a McCrone Micronising Mill<sup>®</sup> to obtain a particle size distribution with D<sub>90</sub> = 15.5 μm (i.e. 90% of the particles have a diameter less than 15.5 μm). The as-prepared, calcined Co/Al<sub>2</sub>O<sub>3</sub> sample was used as a parent batch for the cobalt containing samples; a portion was doped with gold to obtain Au–Co/Al<sub>2</sub>O<sub>3</sub>, while another portion was mixed with Au/Al<sub>2</sub>O<sub>3</sub> to obtain hybrid Au–Co.

The gold catalysts were prepared using an anion exchange technique developed in-house [29]. Using a basis of 10 g of alumina, preparation of Au/Al<sub>2</sub>O<sub>3</sub> was initiated by addition of the support to 1 L of a 0.44 mM solution of chloroauric acid (HAuCl<sub>4</sub>) whose pH had been adjusted to between 4 and 5 by drop-wise addition of a 2 M NaOH solution. The dominant gold chloro-hydroxy complex present in the pH range is AuCl<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>, which maximises gold deposition due to the stronger bidentate adsorption to the alumina surface [30]. The support and gold solution were contacted (while stirring) for 24 h after which the resultant slurry was filtered and the recovered catalyst flushed using 1 L of deionised water. Thereafter, the catalyst was contacted with a 0.5 L 25 wt.-% aqueous ammonia solution for 20 min while stirring, followed by the final washing step which involved flushing the sample recovered from the ammonia wash with 0.5 L of deionised water. An ammonia-washing step was incorporated to allow for substitution of Cl<sup>-</sup> ions with hydroxyl groups and facilitate the removal of weakly bound gold complexes from the alumina surface. Otherwise, the highly mobile, weakly bound gold complexes would result in very large crystallites due to sintering during the calcination process, while Cl<sup>-</sup> ions are a well-known cause of deactivation and have been observed to facilitate sintering of gold crystallites during calcination [30]. Catalyst preparation was terminated after the catalyst was dried in a rotary evaporator at 80 °C and 110 mbar, then calcined in a fluidised bed reactor at 350 °C in air for 6 h.

Preparation of the Au–Co/Al<sub>2</sub>O<sub>3</sub> sample was carried out according to the method described for Au/Al<sub>2</sub>O<sub>3</sub>, but instead using a portion of the Co/Al<sub>2</sub>O<sub>3</sub> parent batch as the support.

The hybrid Au–Co sample was prepared by mechanically mixing Au/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> in a 1/1 mass ratio in order to maintain the same Au/Co atomic ratio in the Au–Co/Al<sub>2</sub>O<sub>3</sub> sample. No further treatment was carried out on the resultant physical mixture.

### 2.2. Catalyst characterisation

The elemental composition of all the prepared catalyst samples in this study was determined using ICP-OES, after dissolving the sample in aqua regia; the digestion process was completed by microwaving the obtained solution for 30 min.

The morphology and the size distribution of the cobalt and gold crystallites was determined using transmission electron microscopy (TEM). TEM analyses were carried out on the calcined and reduced samples using a Zeiss LEO 912-Omega transmission electron microscope and a FEI Tecnai<sup>™</sup> F20 Field Emission TEM coupled with EDS. ImageJ<sup>™</sup> was used to process the obtained micrographs and approximately 100 crystallites were measured in order to obtain the particle size distributions.

XPS scans of the calcined samples were collected using a VG Escalab 200 MKII Spectrometer (Al Kα). Peak identification and deconvolution was carried out using the 'Handbook of X-ray photoelectron spectroscopy' [41] and CasaXPS<sup>®</sup> software, respectively.

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