

Oxidation of CO using gold supported on and NiO/Fe₂O₃ and Fe₂O₃/Co₃O₄ in a hydrogen rich stream for use in fuel cells.

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Introduction

The increase in global population has placed a heavy demand on natural resources and has significantly increased global energy demand [1]. Fossil fuels are by far the most widely used energy source but processing of such fuels results to release of green house gases. In order to address this problem; alternatives to fossil fuels are needed [2]. Fuel cells offer an alternative solution to these challenges [3]. Fuel cells use hydrogen to produce electric power but unfortunately the bulk of the hydrogen used in fuel cells is obtained from reforming processes and contains about 1% CO. CO is known to be detrimental to the platinum electrodes in the fuel cell, especially the polymer exchange membrane fuel cell (PEMFC) and CO must be significantly reduced or totally eliminated. Gold nano particles are now known to be very efficient in the oxidation and preferential oxidation of CO (PROX) if supported either on oxides or mixed metal oxides [4]. Gold was considered an inert metal until Haruta and his team discovered that gold can be very active when supported as nano particles [5].

In this study gold catalysts supported on mixed metal oxides of nickel, cobalt and iron prepared from hydrotalcite like material containing carbonate ions in the interlayer are reported. Hydrotalcites are materials where divalent and trivalent cation hydroxide layers are separated by interlayer anions. They resemble layers such as that of brucite in their structural formulation and posses a general formula $[M_{(1-x)}^{2+}M_x^{3+}(OH)_2](A_{x/n}) \cdot mH_2O$ where $M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}$ and Co^{2+} , $M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$ and V^{3+} with $A = CO_3^{2-}, SO_4^{2-}$ and Cl^- [6]. When these materials are calcined they produce mixed metal oxides of high surface area and specific metal ratio [6]. Mixed metal oxides such as Fe₂O₃/Co₃O₄ and NiO/Fe₂O₃ are investigated as gold support for oxidation of CO in the presence of hydrogen. Oxidation of hydrogen is prevented by carrying out CO oxidation at low temperatures (25-180°C).

Materials and Methods

All chemical used were bought from Aldrich and had 99% purity or more. Hydrotalcite like precursors were prepared from Ni(II) or Co(II) and Fe(III) ions with varying molar ratios at constant pH using coprecipitation method. Precursors of Ni-Fe and Co-Fe were aged at 100 °C in an oil bath for 18 hrs, dried at 110 °C and calcined for two hours at 550 °C and 450 °C respectively. Gold was deposited by deposition precipitation technique using HAuCl₄ as a precursor and the supported catalyst was calcined at 300 °C for four hours. All materials were characterized using XRD, TGA, H₂-TPR, BET, ICP-OES, SEM and TEM. The

feed containing N₂, H₂, CO and O₂ (synthetic air) was used. The percentage composition of the feed was such that CO, H₂ and O₂ were 1%, 50% and 0.5% - 2% respectively and the remainder of the gas being nitrogen. CO₂ (10%) was also introduced as part of the feed to investigate its effect on the oxidation process.

Results and Discussion

XRD results confirmed formation of hydrotalcite like materials. Modification of these materials by calcination produced Fe₂O₃/Co₃O₄ and NiO/Fe₂O₃ mixed metal oxide combinations confirmed by XRD. Gold deposition was confirmed by ICP, SEM and TEM. Particle size distribution analysis confirmed formation of gold nano particles with the range between 3 and 8 nm with the average diameter of about 5 nm. H₂-TPR results of gold containing supports show that reduction peaks of Ni, Co and Fe shift to lower temperatures compared to supports without gold. BET surface areas also decreased as the gold content increased albeit moderately. Catalytic testing at GHSVs of 12 000 h⁻¹, 24 000h⁻¹ and 48 000 h⁻¹ between room temperature and 180 °C shows that CO conversion decreases as the GSHV increase probably due to shorter resident time at higher GHSVs. Gold nano-particles supported on NiO/Fe₂O₃ give high conversions (100 %) but low selectivity to CO₂ (40%) at temperatures as low as 60 °C whereas that supported on Fe₂O₃/Co₃O₄ give conversions around 99% at 120 °C. Selectivity towards CO₂ for Fe₂O₃/Co₃O₄ supported gold catalysts also decrease with increasing temperature. Conversion increases as gold content increases for the catalysts supported on both supports. In fact Fe₂O₃/Co₃O₄ support showed very high catalytic activity all by itself even before gold was supported on it. Time on stream experiments show that the catalysts are stable at least up to 24 hours. Deactivation of the catalysts was observed when CO₂ was introduced to the feed but the catalysts recovered upon switching off of CO₂.

Significance

The results obtained indicate that catalysts are promising low temperature PROX catalyst in view of their activity at low temperatures. This activity is probably due to redox properties of iron and cobalt, in which higher oxidation states reduce to lower oxidation states and vice versa thereby providing oxygen mobility to promote the oxidation of CO. Significant reduction of CO is a good outcome and in line with objective of this project.

References

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