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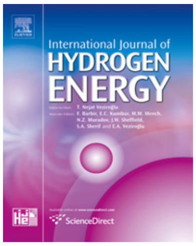

Copper manganite as a catalyst for the PROX reaction. Deactivation studies

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ABSTRACT

$CuMn_2O_4$ nanocatalysts synthesised by silica aquagel confined co-precipitation were analysed for the preferential oxidation of CO at different temperatures and concentration conditions. The catalysts show a higher activity than copper–ceria catalysts synthesised by the same method but, like these, they suffer from slow deactivation during the reaction. Surface analysis (FTIR and XPS) was used to unravel the deactivation mechanisms. Gradual reduction of the catalysts by the carbon monoxide present in the PROX stream was concluded to be the main cause of deactivation.

1. Introduction

Hydrogen streams for fuelling PEM fuel cells need to be almost totally CO-free in order to avoid platinum poisoning. For this reason purification processes, such as preferential CO oxidation, need to be included in the H_2 production process in order to achieve CO concentrations below 20 ppm. Copper-based catalysts have shown good catalytic activity and selectivity for CO oxidation in rich hydrogen streams (PROX reaction) [1,2]. Recent works on the PROX reaction with copper-based catalysts show that the use of nanosized catalysts improves the activity and selectivity of the reaction [1,3,4]. $CuMn_2O_4$, technically known as hopcalite, is a well known oxidation catalyst [5–7] which is employed to remove air pollutants such as carbon monoxide and nitrous oxide from exhaust gas. In CO oxidation, its high activity is usually attributed to the resonance system $Cu^{2+}Mn^{3+}/Cu^{+}Mn^{4+}$ and the high adsorption of CO on Cu^{2+}/Mn^{4+} and of O_2 on Cu^{+}/Mn^{3+} [8,9]. Recently, $CuMn_2O_4$ has been applied in the catalytic steam reforming of methanol [10,11] and preferential oxidation processes [12], with moderate activity and high selectivity at temperatures over 100 °C. Recently developed template methods for synthesising high surface area nanocatalysts have been used to promote a significant increase in their catalytic activity compared to that of their low surface area counterparts. In this area of research, we have demonstrated that the silica aquagel confined co-precipitation method (SACOP) is a useful tool for synthesizing high surface area $CuMn_2O_4$ nanocatalysts providing improved catalytic activity for the methanol steam reforming process [13].

In this work we analyse the activity and stability of nanosized $CuMn_2O_4$ synthesised by SACOP for the PROX reaction. The stability of the catalyst is a parameter that is often disregarded in PROX studies [1], and yet it is of paramount importance for long-term on-board applications. We have also conducted surface studies to unravel the causes of the slow deactivation appreciated in the catalytic tests performed.

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2. Experimental

2.1. Catalyst synthesis

$CuMn_2O_4$ nanocatalysts were synthesised following the SACOP procedure [14]. Basically, $Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ at a 1:2 molar ratio were dissolved in HNO_3. This solution was added dropwise to a mixture of sodium silicate and water at a final concentration of SiO_2:H^+:H_2O = 1:6.54:193.9 and Si/(Cu + Mn) = 4. After hydrolysis (24 h at room temperature) and condensation (24 h at 100 °C) a silica aquagel containing widely dispersed metallic cations was formed. To prevent the cations from leaching during washing, precipitation inside the gel was performed using powdered NaOH. The slurry was repeatedly washed and dispersed in acetone, then filtered, dried at RT and calcined at 550 °C (5°C/min, 4 h). As calcination takes place inside the pores of the silica matrix (confined process) growth of the nanomaterials is restricted and consequently high values of surface area can be achieved [10]. The silica matrix was finally removed by NaOH dissolution (2 M) at ~30 °C over a period of two days.

For comparison reasons, CuO/CeO_2 catalysts were synthesised following the same procedure. A detailed description of the characteristics and the behaviour of these catalysts under PROX reaction can be found elsewhere [4].

2.2. Catalyst characterization

The composition of the catalyst was evaluated by SEM-EDX analysis (DSM 942, Zeiss). XRD was performed in a Siemens D5000 diffractometer to obtain the phase composition. The crystal size of the catalysts was determined by applying Scherrer's equation. The BET surface area was evaluated by N_2 physisorption at −196 °C in an ASAP 2010 analyser (Micromeritics).

Ex-situ X-ray photoelectron spectroscopy (XPS) was carried out by means of a Specs spectrometer, using Mg-K_α (1253.6 eV) radiation emitted from a double anode at 50 W. The binding energies of the spectra obtained were corrected using the binding energy of adventitious carbon (284.6 eV) in the C1s region. The backgrounds were subtracted by means of Shirley baselines, except for the Cu2p3/2 region (linear baseline). All the analysed regions were deconvolved by mixed Gaussian–Lorentzian functions (90:10). For the quantitative analyses the atomic sensitivity factors stored in the CasaXPS database (v2.3.12Dev6) were used.

Ex-situ FTIR spectra of the materials compressed in discs with KBr were recorded on a Nicolet Magna IR-560 spectrometer fitted with a DTGS KBr absorbance detector. The analysed regions were deconvolved by mixed Gaussian–Lorentzian functions (90:10).

2.3. Catalytic activity tests and step-response experiments

Catalytic activity tests were performed during the PROX reaction by using a quartz reactor of 7 mm internal diameter inserted inside a vertical furnace. The catalyst sample (15–30 mg) was diluted in inert SiC particles (285–270 mg) and placed in the reactor between two zones of glass wool, thus ensuring isothermal and plug-flow conditions. Any water present in the exit gases was removed with $Mg(ClO_4)_2$. Analyses of H_2, CO, CO_2, O_2 and N_2 in the product gases were then carried out using a gas chromatograph (HP 6890) equipped with a TC detector.

Two different sets of reaction conditions were applied: (a) "LC" conditions (low concentration): 300 ppm CO + 300 ppm O_2 + 1% H_2 in He (total flow rate = 300 mL/min, STP) and (b) "HC" conditions (high concentration): 0.5 vol% CO + 0.5 vol% O_2 + 25% H_2 in He (total flow rate = 200 mL/min, STP). In both cases the values of the spatial velocities were very high (LC: $0.4 \times 10^{-5}\ mol_{CO}\ g_{cat}^{-1}\ s^{-1}$, HC: $2.3 \times 10^{-5}\ mol_{CO}\ g_{cat}^{-1}\ s^{-1}$). Before the reactions each sample was pre-treated in a helium flow at 200 °C for 1 h. Long duration isothermal experiments were performed for all samples, but in specific cases non-isothermal experiments at decreasing temperatures and pseudo-steady state conditions (~1–2 h per temperature point) were also carried out.

The conversion of CO was evaluated as

$$X_{CO} = 1 - \frac{[CO]_{out}}{[CO]_{in}} \qquad (R1)$$

where in and out refer to the inlet and outlet gaseous stream respectively. The selectivity towards CO oxidation was estimated as:

$$S = \frac{0.5 \cdot ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \qquad (R2)$$

The reaction rate was calculated by means of the Langmuir-Hinselwood mechanism proposed by Liu and Flytzani-Stepahopoulus [15] for CO oxidation over a copper–ceria catalyst, as described elsewhere [1].

Additionally, step-response experiments (LC conditions) were performed in the quartz reactor using different gas mixtures (300 ppm CO/He, 300 ppm CO+ 1% H_2/He and 300 ppm CO_2+ 1% H_2/He) in order to assess the deactivating potential of the gases involved in the PROX reaction over the diluted catalysts.

XPS and FTIR analyses were carried out on the catalyst samples which were labelled as: (1) "Fresh": the fresh sample (as synthesised catalyst), (2) "Pre-treated": the catalyst subjected to He pre-treatment at 200 °C (3) "PROX-1h": the catalyst subjected to He pre-treatment at 200 °C followed by the PROX reaction at 175 °C for 1 h (HC conditions) and (4) "PROX-20 h": the sample pre-treated and subjected to the PROX reaction at 175 °C for 20 h (HC). To avoid external influences between the preparation of each sample and its analysis, the catalysts were cooled down after the reaction in a helium flow and quickly retrieved from the glass wool. All the samples were stored in a vacuum vessel until the XPS and FTIR analyses were performed. Ex-situ techniques permit to determine the presence of stable species formed on the surface of the catalysts that are the cause of deactivation, although no information for intermediate reaction species is given. Ex-situ techniques for the study of deactivation have been successfully employed in a previous work [4].