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Pyrophoricity and stability of copper and platinum based water-gas shift catalysts during oxidative shut-down/start-up operation

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ABSTRACT

The pyrophoricity of Cu/ZnO-based and Pt-based catalysts was studied during oxidative shut-down/ start-up of the low-temperature water-gas shift (LT-WGS) reaction to assess whether these catalysts are suitable for fuel cell application. The Cu/ZnO-based catalysts were observed to display high levels of pyrophoricity manifested as a sharp temperature rise of the catalyst bed upon air introduction. This promoted severe sintering of the bulk and metallic phases of the catalyst facilitating catalyst deactivation. No pyrophoricity was observed for any of the Pt-based catalysts; however, sintering of the metallic phase in Pt/TiO₂ and Pt/ZrO₂ persisted, leading to a decrease in activity. It was likely that the sintering of Pt occurred during LT-WGS operation itself. In contrast, Pt/CeO₂ was the only catalyst which retained its activity, displaying no loss in specific surface area or metal dispersion throughout the entire process making it the most suitable candidate of the materials investigated for fuel cell systems. Temperature-programmed oxidation studies indicated deactivation by the oxidative shut-down/startup operation did not result from the build-up of carbonaceous species.

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1. Introduction

The water-gas shift (WGS) reaction $(CO+H_2O\leftrightarrow CO_2+H_2)$ is useful for conditioning hydrocarbon reformed gas for fuel cells because of its ability to remove CO, which is a poison to the Pt electrodes in fuel cells (Larminie and Dicks, 2000; Trimm and Onsan, 2001), while at the same time generating additional hydrogen (Bartholomew and Farrauto, 2006). The industrial WGS process is carried out in two stages to overcome the thermodynamic and kinetic limitations of the reaction to achieve high CO conversion (Bartholomew and Farrauto, 2006; Thomas, 1970). The two steps involve a high-temperature (350-500 °C) shift over Fe₂O₃/Cr₂O₃ catalysts followed by a low temperature (200-250 °C) shift (LT-WGS) over Cu/ZnO/Al₂O₃ catalysts (Bartholomew and Farrauto, 2006). However, this configuration is not economically feasible for fuel cell type operations (Trimm, 2005) encouraging efforts to develop alternate systems which can operate at LT-WGS conditions. One such advance that generates substantial interest is the development of fuel-cell powered vehicles. However, safety in relation to their operation is very important, such that the hazards to be considered include those associated with fuel and hydrogen. Due to the shut-down/start-up operation that fuel-cell vehicles will be subjected to, hazards possibly arising from pyrophoric catalysts have been recommended for consideration by others (Trimm and Onsan, 2001).

The most intensively studied catalysts for the LT-WGS reaction are Cu/ZnO (Shishido et al., 2006a; Spencer, 1999; Yahiro et al., 2007), and Pt- (Azzam et al., 2007b; Gonzalez et al., 2008; Graf et al., 2009) and Au-loaded (Kim and Thompson, 2006; Rodriguez et al., 2007) metal oxide catalysts. Metal oxide supported Pt and Au catalysts are reported as promising LT-WGS catalysts compared with conventional Cu/ZnO as they are resistant to chlorine and sulphur poisoning, robust and stable in terms of frequent shutdown/start-up type operations common during fuel cell operation and are not pyrophoric (i.e. temperature rise in the catalyst bed due to spontaneous ignition under an oxidative environment) (Azzam et al., 2007a; Fu et al., 2005, 2003; Thinon et al., 2008).

Precious metals supported on the following oxides are the most effective LT-WGS catalysts (Thinon et al., 2008) and are ranked from descending order in terms of activity: Pt ($TiO_2 > CeO_2 > ZrO_2$) (Azzam et al., 2007a; Panagiotopoulou and Kondarides, 2006; Thinon et al., 2008) and Au ($CeO_2 > TiO_2 > Fe_2O_3 > ZrO_2$) (Burch, 2006; Park et al., 2009; Thinon et al., 2008). Unfortunately, they can be prone to thermal instability and rapid deactivation similar to most Cu catalysts. Fu et al. (2005) reported the deactivation of Au/CeO₂ during LT-WGS operation was due to both the loss of CeO₂ support area during steady-state reaction and the formation of cerium oxide-hydroxycarbonate (a reaction inhibitor) during shut-down/start-up operation from water condensate. Kim and Thompson (2005) also

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found the formation of thermally stable carbonate species covering the surface of Au/CeO₂, which blocked the active sites. Denkwitz et al. (2007) elaborated that the carbonate was of monodentate carbonate species which predominately inhibited the LT-WGS reaction, while their formation was enhanced by CO₂ in the feed gas (Denkwitz et al., 2007; Karpenko et al., 2007). Pt/TiO₂ is also unstable as sintering of the active Pt metal sites happens readily during LT-WGS operation (Azzam et al., 2007a, 2008; Zhu et al., 2009).

It is well documented that Cu/ZnO-based catalysts are susceptible to sintering, the primary cause of deactivation (Shishido et al., 2006a, 2006b). Shishido et al. (2006b) showed that the stability of Cu/ZnO catalysts was dependent on the initial H₂ pretreatment, and the sintering of Cu particles was the main source of catalyst deactivation. Guo et al. (2009) reported that the shut-down/startup cycles during LT-WGS operation did not affect the activity of Cu/ZnO-based systems even when water was condensed on the catalyst during the shut-down period. They argued that deactivation of the Cu/ZnO/Al₂O₃ catalyst was mainly attributed to the loss of active sites from the formation of carbonate species rather than the sintering of Cu crystallites (Guo et al., 2009).

This study investigates the activity and stability of Cu/ZnO-based catalysts, including those loaded with refractory oxides such as Al₂O₃ and La₂O₃, and Pt-based catalysts during oxidative shut-down/startup LT-WGS operating conditions. Cu/ZnO-based catalysts have been previously observed as pyrophoric while Pt-based catalysts are not; however, the effect of pyrophoricity on catalyst characteristics and subsequent LT-WGS performance has not been systematically investigated. The knowledge gained here allows for assessment of the suitability of these catalysts for fuel cell application.

2. Experimental

2.1. Catalyst preparation

A flame spray pyrolysis (FSP) reactor (Teoh et al., 2005) was used to synthesize Cu/ZnO, Cu/ZnO/La₂O₃, Cu/ZnO/Al₂O₃, Pt/TiO₂, Pt/CeO₂ and Pt/ZrO₂ particles. The Cu loading was maintained at approximately 37 wt%, with La loaded at 2.3 wt%. The Cu/ZnO/Al₂O₃ catalyst (F-COM) was fabricated based on a typical commercial catalyst composition with weight ratio of 37:55:8, respectively (Gines et al., 1995). Pt loading was maintained at approximately 1 wt% of their respective oxide supports. In the case of copper based catalysts, precursor solutions containing predetermined amounts of metal oxides with a total molar concentration of 0.5 M were prepared by mixing zinc 2-ethylhexanoate (Alfa, purity >99%), lanthanum (III) 2-ethylhexanoate (10 wt% in hexane solution, Aesar), aluminium s-butoxide (Strem, purity >98%), and a copper 2-ethylhexanoate (Aldrich, purity > 99.9%) in xylene (Riedel de Haen, 96%). For platinum based catalysts, precursor solutions of titanium(IV) isopropoxide (TTIP, 97% purity, Aldrich), cerium(III) 2-ethylhexanoate (49 wt% in 2-ethylhexanoic acid, Strem), zirconyl 2-ethylhexanoate (Strem) and platinum(II) acetylacetonate (Aldrich, purity >97%) were used. During FSP synthesis, the liquid precursor was fed (rate: 5 ml min^{-1}) to the flame by a syringe pump (Inotech R232). The generated particles were collected on a glass fibre filter (Whatmann GF/D) with the aid of a vacuum pump (Alcatel). Detailed descriptions on other operating conditions can be found elsewhere (Teoh et al., 2005). La₂O₃ (Aldrich, 99.9%) was used as the La reference in this study.

2.2. Catalyst characterization

X-ray diffraction (XRD) spectra were collected on a Philips X'Pert MPD instrument using CuK α (λ =1.542 Å) with scan range from 20° to 90° at a scan rate of 0.22° min⁻¹ and step size of 0.026°.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the metal content in each synthesized sample. The measurements for Cu catalysts were performed on a Perkin-Elmer OPTIMA DV3000 apparatus and for Pt catalysts, a Varian Vista-MPX. Cu/ZnO samples were dissolved in nitric acid (3 M) before measurement and Pt samples were dissolved in an acid mixture of nitric, hydrochloric and hydrofluoric with 2:6:5 volume ratios, while being heated at 180 °C until solution was near dryness. The resultant solution was then cooled and made to volume with a 5% hydrochloric acid matrix before ICP-OES analysis. Copper metal surface area (CSA) was determined by the N₂O decomposition method at 90 °C using the same experimental methodology reported by Jensen et al. (2004). assuming a reaction stoichiometry of two Cu atoms per N₂ molecule and a Cu surface density of 1.46×10^{19} atom m⁻² (Evans et al., 1983). Prior to the measurement, 30 mg of sample was reduced at 230 °C for 30 min and flushed with He (50 mL min⁻¹) for a further 30 min. The dispersion and sizes of the Pt deposits were determined by CO pulse chemisorption using a Micromeritics Autochem 2920 instrument. The Pt/oxide samples were first reduced in 50 ml/min of 10% H₂/N₂ for 60 min at 300 °C followed by flushing with 50 ml/min of He at 310 °C for another 60 min. Pulse injections (0.5 ml of 10% CO in He) were introduced at 30 °C for Pt/TiO2 and Pt/ZrO2 assuming a Pt:CO stoichiometric ratio of 1:1 (Strobel et al., 2003). For Pt/CeO₂ the CO chemisorption was carried out at -80 °C by immersing the sample cell in an isopropanol and liquid nitrogen mixture. This ensured the CeO₂ oxide did not interfere with the chemisorption (Tanabe et al., 2009). Dispersion of the Pt deposits is defined as the ratio of the atoms accessible to the CO relative to the total number of Pt atoms in the system. The specific surface areas (SSA) of the prepared catalysts were analysed by nitrogen adsorption at 77 K, on the Micromeritics Tristar 3000, using the BET model.

2.3. Catalyst activity

Activity testing was carried out using a 6 mm I.D. stainless steel packed bed reactor with as-prepared catalyst sample (100 mg) diluted with α -Al₂O₃ (70 μ m, 500 mg). Prior to the activity test, catalysts were reduced under a total flow of 100 mL min $^{-1}$ (10% $H_2/N_2)$ for 1 h at 230 °C and flushed with N₂ for 30 min before returning to ambient temperature. The standard test stream of 100 mL min⁻¹ discharging at atmospheric pressure, comprised 7% CO, 8.5% CO₂, 23% H₂O, 37.5% H₂ and 25% N₂ (Coregas) to which deionised water was added via a vaporizer fed by a high precision syringe pump (ISCO Inst., model 260D). The above conditions corresponded to a gas hourly space velocity of $11\,000$ h⁻¹. Operating temperature ranged from 150 to 300 °C with 50 °C increments at 10 °C min⁻¹. The gases were fed by mass flow controllers (Brooks). The product stream, after passage through an ice trap to remove water, was analysed using two gas chromatographs (Shimadzu GC8A) fitted with thermal conductivity detectors. One chromatograph was operated with helium passing through a 1.8-m CTR I column (Alltech Associates, Inc) for analysis of CO₂, CO, N₂, O₂ and CH₄. The other used argon passing through a 2 m molecule sieve 13X column (Alltech Associates, Inc.) for H₂ analysis. CO conversion was removed from thermodynamic equilibrium (Chinchen et al., 1988) to induce low residence times and avoid the impact of mass transfer limitations on the results. Further details regarding the calculations for CO conversion are provided in Supporting information (A).

2.4. Cyclic shut-down/start-up operation of catalyst under oxidative environment

This experiment was designed to analyse the pyrophoricity of the catalyst during LT-WGS operation. Cyclic shut-down/start-up operation under an oxidative environment was evaluated after 1 h Download English Version:

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