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Wire gauze and cordierite supported noble metal catalysts for passive autocatalytic recombiner

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HIGHLIGHTS

- Synthesis by electroless deposition method and chemical reduction route.
- Particle size of 0.1–0.5 μm & 3.5–5 nm for Pt–Pd/Wg & Pt–Pd/Cord catalysts.
- Active for H_2 and O_2 reaction with initial H_2 concentration of 1.5 to 7% in air.
- Active in presence of different contaminants like CO_2, CH_4, CO & relative humidity.
- Enhanced resistance of Pt–Pd/Cord catalyst towards the poisoning of CO.

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ABSTRACT

Hydrogen released in nuclear reactor containment under severe accident scenario poses a threat to containment and hence needs to be regulated by catalytic recombination. Mixed noble metal catalysts with platinum–palladium supported on stainless steel wire gauze and cordierite support have been developed for this purpose. The developed catalysts have been found to be highly efficient for removal of hydrogen concentration in the range of 1.5 to 7.0% v/v in air. Though both the catalysts exhibit similar kinetics for lower hydrogen concentration, cordierite supported catalysts exhibits better kinetic rate at higher hydrogen concentration. The performances of these catalysts in presence of various probable catalytic poison like carbon monoxide and catalytic inhibitors like moisture, carbon dioxide, and hydrocarbons provide data for use of these catalysts under the actual scenario. Compared to stainless steel wire gauze supported catalyst, the cordierite based catalyst are found to exhibit enhanced resistance towards carbon monoxide and limited temperature rise for safer application at higher hydrogen concentrations.

1. Introduction

In nuclear reactor large amount of hydrogen is generated during loss of coolant accident followed by Emergency Core Cooling System (ECCS) failure. The origin of hydrogen generation is mainly metal/clad – steam reaction and molten core – concrete interactions (MCCI). The hydrogen concentration in reactor containment could exceed the flammability limits (4.5% in air) in such a scenario. Fast kinetics and self-propagating nature of metal-steam reaction results in fast shoot up in hydrogen concentration in a very short period of time (Lewis, 1988; Prabhudharwadkar et al., 2011). Radiolysis of water is also another source of hydrogen which leads to further increase in hydrogen concentration in containment over longer period of time. As hydrogen concentration in air exceeds 8% v/v, it could lead to severe threat to the containment integrity due to deflagration or explosion (IAEA-TECDOC-1661, 2011). Thus, hydrogen concentration needs to be controlled to safeguard integrity of the reactor containment and to thwart radioactivity fallout and its adverse impact on environment (Della Loggia, 1992; Boeck, 2001). If we look in to the past of nuclear power plants accidents, Three mile Island (US) and Fukushima (Japan) have suffered from endanger of hydrogen explosion (Srinivasan and Gopi Rethinarajn, 2013; Ahin and Sarwar, 2013). To avoid this kind of situation there is need to address the hydrogen risk and a lot of effort has been put in by the concerned nuclear organizations worldwide. Several alternatives have been proposed for dealing with this issue viz. pre and post inerting, deliberate ignition system, dilute venting, and passive autocatalytic recombiner (Reinecke et al., 2004; Brockerhoff et al., 2000; Fineschi et al., 1996). Passive autocatalytic recombiner (PAR) is one among the several promising options to deal with this

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situation. It has intrinsic advantages over other options, that it can be auto initiated, does not depend on external power supply or other support for the operation, it can be placed at any location in containment and it can be operated without personal specific attention. (Ledjeff, 1987; Chakraborty, 1988; Bachellerie et al., 2003). Several types of catalysts with different noble metals like Platinum (Pt), Palladium (Pd) on various supports such as alumina, stainless steel plates, silica, γ-alumina, porous titanium plates and cordierite honeycomb have been studied in details by several research groups and found to be effective for H_2 and O_2 recombination reaction (Morfin et al., 2004; Shepelin et al., 2012; Payot et al., 2012). These catalysts are expected to remain in the containment for long time before their actual use, if at all during LOCA, and hence should be resistant to prospective catalytic poison like carbon monoxide (Klauck et al., 2014) and inhibitor like carbon dioxide, water vapour and hydrocarbon etc. Chemistry Group, BARC has been actively involved for development of catalysts to meet the specification of PAR (Sanap et al., 2011; Belapurkar et al., 2008). High surface area catalysts are susceptible to catalysts poisoning due to water vapour which is the reaction product of hydrogen–oxygen recombination reaction. Stainless steel (SS) wire gauze and cordierite ceramic supports are having very low surface area and they fit in the specification of this kind of catalysts preparation. It has been also well reported that bimetallic catalysts, due to their synergic effect and remarkable changes in electronic structure, have advantage over their individual counterparts (Sinfelt, 1973; Toshima and Yonezawa, 1998). Hence, for this purpose we developed bimetallic Pt–Pd/wire gauze and Pt–Pd/cordierite ceramic supported catalysts. Electroless deposition method using formaldehyde as reducing agent has been employed to prepare wire gauze supported Pt–Pd bimetallic catalysts (Rao and Trivedi, 2005). Chemical reduction route using hydrazine hydrate as reducing agent has been attempted for the synthesis of cordierite supported Pt-Pd bimetallic catalysts (Lin et al., 2007). Prepared catalysts have been characterized for their noble metal loading, phase purity, particle size and morphology. The catalysts were evaluated for the catalytic activity for various concentrations of H_2 in air and in presence of probable poison like carbon monoxide and catalytic inhibitor like carbon dioxide, methane and relative humidity etc.

2. Catalyst preparation and characterization

In present study, stainless steel (SS) wire gauze with the dimensions of 12 cm × 16 cm and cordierite ceramic plates with dimensions of 5 cm × 16 cm × 2 cm were exploited as support. Chloroplatinic acid (Hindusthan Platinum Private Ltd, 39.8% Pt) and palladium chloride (Johnson and Matthey, 60% Pd) were used as noble metal precursors. Hydrazine hydrate (Spectrochem, 99.8%) and formaldehyde (Thomas Baker, 37–41 W/V%) were employed as reducing agent.

2.1. Wire gauze based catalyst

Pt–Pd on SS wire gauze based catalysts has been prepared by electroless deposition method using formaldehyde as reducing agent. Electroless bath with known concentrations of chloroplatinic acid (9.5 mg/ml Pt) = 25 ml, palladium chloride (12 mg/ml Pd) = 5 ml and formaldehyde (1:10 diluted) = 120 ml, has been prepared with further dilution to 5000 ml by distilled water in a 5 l beaker. Four pieces of wire gauze were allowed to make rotate with the help of motor (1 rpm) in this bath. As coating proceeds on wire gauze, colour of bath solution changed from dark yellow to colourless.

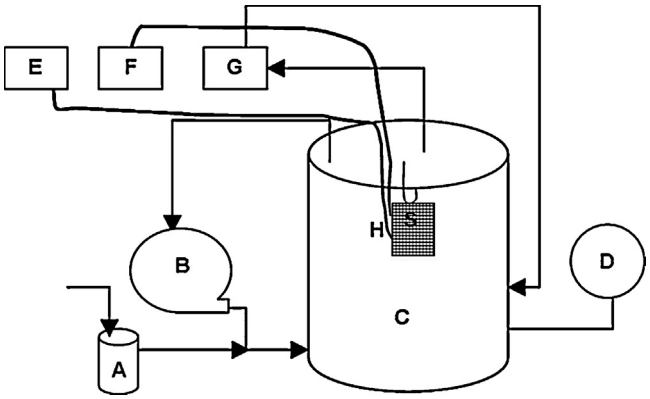

Fig. 1. Experimental set up for catalytic activity, (A) fixed volume injector (0.25 L), (B) air circulating pump, (C) Stainless Steel reactor (40 L), (D) pressure gauge, (E) and (F) mV meters, (G) hydrogen monitor, (H) thermocouples, and (S) catalyst sample.

Following reactions takes place on wire gauze–solution interface during the time of noble metal deposition.

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^- \qquad E = 0.057\,V$$

$$Pd^{2+} \quad or \quad Pt^{2+} + 2e^- \rightarrow Pd(0)\,or\,Pt(0)$$

$$E = 0.915\,V\,(Pd), \quad 0.726\,V \quad (Pt)$$

The noble metal loading observed is in the range of ~60–80 mg on each wire gauze sample. The catalyst with 80 mg (0.8% w/w) loading has been considered for detailed study and it has been denoted as Pt–Pd/Wg.

2.2. Cordierite based catalyst

Chemical reduction route has been attempted for the synthesis of cordierite based Pt-Pd bimetallic catalysts. Chloroplatinic acid (10 mg/ml Pt) = 4 ml and palladium chloride (10 mg/ml Pd) = 2 ml were mixed homogenously and applied on the surface of previously cleaned and dried cordierite plate. The plates on which precursor solution was applied were dried at 180 °C for 2 h. Decomposition of precursors applied plate was carried out at 350 °C for 3 h before its reduction in solution of diluted hydrazine hydrate. Following reactions take place during the step of reduction.

$$H_2PtCl_6 + N_2H_5OH \rightarrow Pt^0 + 6HCl + H_2O + N_2(\uparrow)$$

$$PdCl_2 + N_2H_5OH \rightarrow Pd^0 + 2HCl + H_2O + 1/2H_2 + N_2(\uparrow)$$

The observed noble metal loading is of 60 mg (0.2% w/w) and the sample is denoted as Pt–Pd/Cord.

2.3. Characterization

The crystalline phase purity of deposited noble metal has been assessed by powder X-ray Diffractometer. The XRD patterns were recorded with Philips analytical instrument with Ni filtered Cu-*K*-α radiation in the scanning range of 10–70° two theta value. Surface morphology and particle size of deposited nanoparticles were analysed using Scanning Electron Microscopy (JEOL JSM-6360) and Field Emission—Scanning Electron Microscopy (FE-SEM, JEOL INSTRUMENT-7600F with an accelerating voltage of 5 kV). For cordierite ceramic samples charging was reduced with gold–palladium sputter coating using a current of 10 mA for 5 min.

2.3.1. X-ray diffraction

XRD pattern recorded for different samples are shown in Fig. 2. XRD patterns of bare wire gauze and Pt–Pd/Wire gauze sample are shown in Fig. 2a and b, respectively. As seen from this data, the