



Nanostructured Pd modified Ni/CeO₂ catalyst for water gas shift and catalytic hydrogen combustion reaction

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ABSTRACT

Nanostructured Pd-modified Ni/CeO₂ catalyst was synthesized in a single step by solution combustion method and characterized by XRD, TEM, XPS, TPR and BET surface analyzer techniques. The catalytic performance of this compound was investigated by performing the water gas shift (WGS) and catalytic hydrogen combustion (CHC) reaction. The present compound is highly active and selective (100%) toward H₂ production for the WGS reaction. A lack of CO methanation activity is an important finding of present study and this is attributed to the ionic substitution of Pd and Ni species in CeO₂. The creation of oxide vacancies due to ionic substitution of aliovalent ions induces dissociation of H₂O that is responsible for the improved catalytic activity for WGS reaction. The combined H₂-TPR and XPS results show a synergism exists among Pd, Ni and ceria support. The redox reaction mechanism was used to correlate experimental data for the WGS reaction and a mechanism involving the interaction of adsorbed H₂ and O₂ through the hydroxyl species was proposed for CHC reaction. The parity plot shows a good correspondence between the experimental and predicted reaction rates.

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1. Introduction

<Hydrogen is considered as the most efficient and environmentally benign energy fuel. It allows additional flexibility in the selection of energy resources and could play a major role mitigating effects of climate change [1]. Water gas shift (WGS) reaction is one of the key steps in hydrogen production for ammonia and Fischer-Tropsch synthesis [2]. Due to recent developments in the fuel cell technology, WGS reaction is also used in the energy power generation systems for CO-free hydrogen production. WGS reaction not only mitigates CO concentration but also increases the hydrogen content of reformer stream. WGS reaction is mildly exothermic and equilibrium limited. Therefore, in industry, WGS reaction is carried in two stages, namely high temperature shift over Fe₃O₄/Cr₂O₃ at 350–500 °C and low temperature shift over Cu/ZnO/Al₂O₃ at 200–250 °C for high activity and CO conversion [3,4]. However, the commercially available catalysts used in two stage processes are not suitable for hydrogen production because of their cumbersome activation procedure, sensitivity to start-up/shut-down cycles and pyrophoricity [5]. It is of great interest to develop highly active, selective, cost effective, thermally stable and non pyrophoric WGS catalyst.

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Ceria, as support, offers unique properties due to its oxygen storage capacity (OSC) for reactions such as three-way automotive catalysts [6], preferential CO oxidation [7], and catalytic oxidation of hydrocarbons [8,9]. The addition of noble/transition metal at low concentration alters the redox and catalytic properties of ceria based compounds [10–12]. The noble metal (Au, Pt, Rh, Pd etc.) modified CeO₂, TiO₂ and ZrO₂ are receiving widespread attention as low temperature WGS catalysts [13–17]. However, the cost of noble based catalysts makes them detrimental for large scale applications. Further, these catalysts are bifunctional whereby CO adsorbs on the metal and the dissociation of H₂O take place over ceria support [18]. The low activation energy barrier for the dissociation of H₂O and low adsorption energy of CO are the key factors for the developments of low temperature WGS catalyst [19]. Therefore, the creation of oxide ion vacancies are desirable for dissociation of H₂O molecules [20]. The substitution of aliovalent ions in the form of M²⁺/M³⁺ not only create vacancies but also induce redox couples in the substituted metals as well as in ceria and renders strong metal support interactions.

The performances of bimetallic catalysts are often superior to those of monometallic materials [21,22]. The higher flexibility in chemical composition and interatomic arrangement compared to monometallic materials can render a new reaction pathway [23]. Previously, we have reported improvement in the activity and selectivity of bimetallic catalysts for WGS reaction [24]. Recently, it has been shown that Cu/Pt and Cu/Pd modified ceria are promising candidates for low temperature WGS reaction [25,26].

Monometallic Cu/CeO₂ and Ni/CeO₂ are also highly active and competitive for noble metal supported catalysts [27]. Further, Ni is more reactive toward H₂O than Cu in WGS reaction [28]. Therefore, the exploration of bimetallic catalyst based on Ni is desirable for the low temperature shift reaction. The improvement in the stability and activity of Ni supported catalysts is manifested on the addition of metal such as Rh, Cu, Pt, Pd, Mo and Co for reforming reactions [29,30]. However, the evaluation of the performance of such catalysts toward WGS reaction for hydrogen production has not been reported in the literature. Thus, it is of interest to investigate Pd modified Ni/CeO₂ ionic bimetallic catalyst for WGS reaction.

It is impractical for most of the polymer electrolyte membrane (PEM) fuel cells to consume all hydrogen and recycling of unused mixture of hydrogen and carbon dioxide is the usual method to make the operation economical. However, recycling of exhaust builds up the concentration of CO₂ in the system, which consequently dilutes the fuel gas leading to lower the performance of fuel cell. Therefore, it is imperative to treat the exhaust of fuel cell for removal of hydrogen. The exhaust from the PEM fuel cell can be sent to a waste hydrogen burner and heat recovery steam generator to produce steam for further utilization. Thus, direct combustion of H₂ is a common way to extract energy contained in H₂. However, catalytic hydrogen combustion (CHC) offers some advantages over direct combustion of H₂. CHC reaction can be carried out over a catalyst at lower temperatures compared to thermal oxidation and the removal of H₂ even at low concentrations is possible by catalytic oxidation [31]. The applications of CHC reactions are also prevalent in various other systems. One such application involves the prevention of destructive explosion in nuclear reactor. H₂ acts as reducing agent in various reactions such as selective catalytic reduction (SCR) of NO [32], hydrogenation of alkenes [33] etc. CHC reaction is also an integral part for the preferential oxidation (PROX) of CO in H-rich gas that used for the purification of feed gas for PEM fuel cell [34]. Detailed applications of CHC in different systems can be found in our previous study [35]. Further, the recombination of H₂-O₂ is a fundamental catalytic oxidation reaction. Therefore, the catalytic performance of the synthesized compound toward CHC reaction was also studied separately in order to understand the kinetics and mechanism of CHC reaction.

The objective of the present study is to synthesize a bifunctional, bimetallic catalyst with high activity and selectivity for WGS reaction. Therefore, Pd modified Ni/CeO₂ catalyst was synthesized by single stage solution combustion and characterized by XRD, TEM, XPS, TPR and BET surface analyzer techniques. The activity of synthesized compound toward WGS and CHC reactions was investigated and steady state kinetics measurements of both the reactions were also carried out over a wide range of temperature. The reversibility of the catalyst in the redox gas treatment is necessary for ceria mediated redox process, and, therefore, cyclic redox behavior of catalysts was also studied using H₂-TPR experiments. Mechanisms for both the WGS and CHC reactions were proposed to correlate the experimental data.

2. Experimental

2.1. Catalyst synthesis and characterization

Pd and Ni substituted CeO₂ was synthesized by a single step solution combustion method. This involves the combustion of a salt of the ceria and a Pd/Ni metal salt with a fuel in a solution. For the synthesis of Ce_{0.88}Pd_{0.02}Ni_{0.1}O_{2-δ}, ceric ammonium nitrate [(NH₄)₂Ce(NO₃)₆], (Nice Chemicals, India), palladium dichloride [PdCl₂ (Merck, India)], nickel nitrate [Ni(NO₃)₂·6H₂O (S.D Fine Chem, India)] and urea (Fisher Scientific, India) as a fuel were taken in the molar ratio of 0.88: 0.02: 0.1: 3.7. The reactants were

dissolved in 30 cm³ water and introduced into a preheated muffle furnace at 400 °C. The solution boiled with frothing, foaming and redox mixture after dehydration, and ignited yielding a voluminous solid product within a few minutes. A similar procedure was followed for the synthesis of Ce_{0.9}Ni_{0.1}O_{2-δ}. Both the combustion products were finely grounded and used for the catalytic reaction.

The catalysts were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD pattern was recorded on a Phillips X'Pert diffractometer using a Cu K α radiation source at a scan rate of 0.02 min⁻¹ in the 2 θ range of 10–80°. JANA 2000 program suite package was used for XRD analysis and profile refinement methodology was used to obtain the structural changes in the CeO₂ on the substitution of Pd/Ni metal ions. The electronic structure of both the catalysts before and after the reaction was determined by XPS on a Thermo Scientific Multilab 2000 system using Al K α radiation (1486.6 eV). Binding energies of core levels of metal ions were adjusted relative to binding energy of C (1s) observed at 285 eV.

The particle size and morphology of catalyst were characterized by TEM analysis. The catalyst powder was dispersed in ethanol using an ultrasound bath and a drop of the suspension was placed on a carbon film covered copper grid (300 mesh sizes). Image and diffraction pattern were obtained on a FEI Technai 20 electron microscope operating at 200 kV. High-resolution (HRTEM) images were also obtained. The surface area of the catalysts was measured by nitrogen adsorption at 77.4 K with SMART SORB 93 model (Smart Instruments Company Pvt. Ltd, India). The catalyst samples were degassed at 150 °C for 5 h prior to the measurement.

2.2. Temperature programmed reduction (H₂-TPR)

Temperature programmed reduction (H₂-TPR) was used to study the effect of Pd and Ni metal substitution on the oxygen storage capacity (OSC) of ceria. Cyclic redox behavior or OSC of both the catalysts were also studied by H₂-TPR or hydrogen uptake. 25 mg of the catalyst sample (50–100 mesh sizes) was plugged with ceramic wool in a quartz reactor of length 30 cm and 0.4 cm ID. The sample was first pretreated in a flow of pure Ar (Chemix, Bangalore, India) at 400 °C for 30 min in order to get a stable baseline and then, H₂-TPR experiment was performed by heating the catalyst sample from 25 to 500 °C at constant rate of 10 °C/min, in a 5% H₂/Ar gas mixture (Chemix, Bangalore, India) with total flow rate of 30 cm³/min. The H₂-uptake during the reaction was measured using a TCD and H₂ consumption was calculated from the area under the curve which was calibrated by the quantitative reduction of known weight of CuO. Therefore, the amount of H₂ uptake or equivalent lattice release was determined.

2.3. Catalytic experiments

Catalytic experiments were conducted in a packed bed quartz reactor tube (30 cm in length and 0.4 cm of ID) operated isothermally at atmospheric pressure, in the temperature range of 60 to 500 °C. All the catalysts were used in the as-prepared form without further activation. 300 mg of catalyst in granules form (170–420 micron) was loaded in the reactor and was diluted by adding the required amount of silica granules of 150–290 micron. The reactor tube was heated from outside using an electric furnace. The temperature was measured by a K-type thermocouple placed at the center of the packed bed, and was controlled by a PID controller. The reactant gases (all supplied by Chemix Bangalore, India) were certified calibration gas mixtures with high purity (99.9%). The

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