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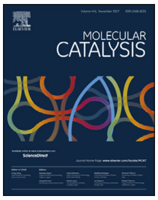

Editor's choice paper

Aluminium and rhodium co-doped ceria for water gas shift reaction and CO oxidation

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ABSTRACT

This study presents the synthesis and application of aluminium and rhodium co-doped ceria for water gas shift (WGS) reaction and CO oxidation. The catalyst was synthesized using single step solution combustion method to obtain porous catalyst of relatively high surface area. The catalyst was characterized by various techniques. All the characterization results revealed successful substitution of the constituent dopants in ceria. The catalyst obtained was tested for its activity for WGS and CO oxidation. The catalyst exhibited higher catalytic activity in comparison to the other noble metal counterparts. A plausible dual site microkinetic model has been proposed in this study for WGS and CO oxidation over Rh/ceria based catalyst and a robust rate expression has been obtained. This rate expression in conjunction with the kinetic parameters and isothermal plug flow reactor model was used to predict the experimental CO conversion. As evident from the simulation results, the kinetic model developed in this study was able to predict the experimental trend with reasonable accuracy for both WGS and CO oxidation.

1. Introduction

With the advent of stringent norms for automotive and industrial emissions, there has been interest in the application of noble metals for automotive exhaust processes mainly in three way catalytic (TWC) converters [1]. On the other hand, with the increase in the demand for high purity hydrogen production from hydrocarbon processing and catalytic reforming applications in industries, there has been increase in search of viable, potential catalysts for selective hydrogen production and purification [2]. CO emissions from the above applications can be effectively reduced with the usage of catalysts with high thermal stability and low temperature activity. Thus an effective catalyst for CO abatement applications should be highly selective for increased hydrogen production and should exhibit increased CO conversions at low temperatures. This requirement has led to the development of noble metal (NM) based catalysts for various CO abatement processes such as CO oxidation, preferential oxidation, and water gas shift (WGS) reaction [2]. Among noble metals, Pt and Rh have been highly effective owing to their higher affinity for CO adsorption thus facilitating their usage for CO abatement processes.

Platinum based catalysts have been explored in the form of impregnation, mono metallic doping [3], bi-metallic doping [4] and alloying techniques for CO oxidation and WGS [5]. However, in comparison with Pt based catalysts, other noble metal based catalysts like rhodium, ruthenium has not been extensively explored for WGS and CO oxidation on industrial scale [4]. Further, the usage of rhodium in conjunction with ceria has not been explored for CO abatement processes [6]. The usage of rhodium doped bimetallic catalysts has not been widely explored for industrial CO abatement processes such as WGS and CO oxidation.

As presented in many studies [7–12], the adsorption and activation of hydroxyl species are the key for low temperature WGS. In this juncture, vacancy formation facilities the effective adsorption of H_2O species and their activation. The usage of reducible supports such as TiO_2, CeO_2 have been studied for the activity for WGS [8]. Among these reducible catalysts, ceria based catalysts are known for their oxygen storage capacity (OSC) and stability till moderate temperatures [13]. However, in recent times, doped ceria catalysts have also been synthesized to enhance the vacancy formation and thus enhancing the OSC [4]. This protocol of doping ceria has led the development of ceria based mono-metallic and bi-metallic noble metal ionic catalysts, which showed higher activity and stability.

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In this study, we have synthesized rhodium based bimetallic catalyst, i.e., rhodium aluminium co-doped ceria using single step solution combustion synthesis. The catalyst obtained has been characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), BET surface area and H_2 temperature programmed reduction (TPR) techniques. The catalyst was tested for its activity for CO oxidation and WGS reaction. In this study, we also present a plausible dual site mechanism for CO oxidation and WGS based on redox mechanism developed in our previous study [14]. The kinetic parameters proposed are then validated against the experimental data obtained using the rate expressions developed for the redox mechanism.

2. Experimental section

2.1. Material synthesis

The synthesis procedure involves the solution combustion synthesis (SCS) protocol described in earlier studies [15,16] where appropriate quantities of Al, Rh, Ce precursors i.e., aluminium nitrate nona hydrate(Merck), rhodium chloride hydrate (Merck), and ammonium cerium nitrate (Merck), along with urea, based on their relative substitution fractions were dissolved in 15 mL of D.I H_2O to prepare a homogenous solution. This solution was then transferred to the heating chamber of muffle furnace maintained at 400 °C. The combustion process initiated with the evaporation of H_2O with spontaneous ignition, combustion of mixture and emission of product gases leaving a solid porous material brick- red in texture as the end product. Note that aluminium and rhodium co-doped ceria will be referred hereafter as CAR.

2.2. Experimental procedure for catalytic activity

The catalyst (CAR) was tested for its activity for CO oxidation and low temperature water gas shift (WGS) reaction. For this differential reactor proximity has been followed i.e., the catalytic loading was taken to be 15 mg, 30 mg and 75 mg for CO oxidation and 25 mg, 50 mg, 100 mg and 200 mg for WGS. The dry gas flow rate has been maintained at 100 mL/min for CO oxidation and WGS. The inlet gas composition for CO oxidation was 2.4 vol% CO, 2.4 vol% O_2 and rest N_2. The gas composition was 2 vol% CO and H_2O for the WGS reaction was supplied at 0.05 mL/min using HPLC (Waters® model 515), vaporized through a boiler, exit steam from which is sent to the reaction chamber (4 mm I.D quartz tube). The reactor consists of catalyst plug at its centre held using ceramic wool at both ends. The catalyst bed is made of the individual loadings of the catalyst pellets of (150–300 μm) mesh size diluted with silica beads to maintain isothermal conditions along the catalyst bed of 1 cm. The experimental setup also consists of a moisture trap to condense excess unreacted steam from the reactor outlet. The exit gas composition from the reactor outlet devoid of moisture was analysed through a gas chromatograph (GC) (Model: Nano GC, Mayura Analytical Pvt. Ltd.). The GC used in this study is equipped with a flame ionization detector (FID) to interpret the relative concentrations of the carbon based species and thermal conductivity detector to measure the relative concentrations of hydrogen in the product stream. The temperature of the catalyst bed was maintained at steady state conditions across the experimental temperature range using, a PID equipped feedback controller (Care systems®, Bangalore) attached to the furnace. Differential reactor approach has been used in this study to approximate the experimental rate of reaction. This approach includes the variation of catalyst loading i.e. weight of the catalyst keeping the flow-rate of the inlet gas constant. The rate of reaction is thus approximated from the fractional conversion of the limiting reactant which in the present study is CO.

3. Characterization of the catalyst

3.1. X-ray diffraction (XRD)

The obtained catalyst after synthesis is calcined for 2 h at 400 °C. The material obtained after calcination is characterized using X-ray diffraction. For this Rigaku X-ray diffractometer with CuKα as radiation source at 40 kV and 30 mA was used.

3.2. X-ray photoelectron spectroscopy

The X-ray photoelectron spectra (XPS) of the catalyst was obtained using AXIS ULTRA instrument with Al Kα source. The binding energies of constituent elements were corrected based on adventious carbon binding energy of 284.8 eV.

3.3. BET surface area

The catalyst was heated at 150 °C for 2 h, This process was used to remove any moisture present in the catalyst. The obtained catalyst was then used to obtain the BET surface area using Belsorb® surface area analyser.

3.4. H_2 TPR studies

The H_2- temperature programmed reduction (TPR) was performed to quantify the oxygen storage capacity of the catalyst. For this, 10 mg of the catalyst was taken in centre of a quartz reactor. The catalyst was held firmly by ceramic wool plugs inserted at both ends. Hydrogen-argon mixture (5 vol% H_2 + 95 vol% Ar) was passed through the catalyst bed at 30 mL/min. The temperature of the catalyst bed was increased at 10 °C/min. The change in the thermal conductivity of the effluent gases from the reactor was measured using thermal conductivity detector (TCD).

4. Mechanism and modelling of WGS for Rh doped ceria

The mechanistic studies for WGS over Rh [17,18] impregnated on non-reducible supports propose the reaction pathway for WGS predominantly with the decomposition of the surface carboxyl species to be the rate determining step of the mechanism. Despite the accurate predictions of the detailed kinetic models for WGS over Rh/non-reducible supports [17,18], the predictions of the mechanism based on Rh metallic site alone for estimating the equilibrium of WGS for Rh/ceria deviate significantly from the experimental observations [19]. This was attributed to the non-inclusion of the surface vacancies and the OH species contribution by ceria based vacancies in the reaction mechanism. On the other hand, X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) based studies probing the insights of the reaction mechanism of WGS on Rh/ceria, propose vacancies to contribute significantly for H_2O adsorption and H_2 formation. This is also reflected from the steam activation and hydrogen production studies [20].

The earliest spectroscopic insights for WGS over Rh/ceria [21] contained a detailed overview of the TPD and spectroscopic spectra of different adsorbed species such as CO, CO_2, H_2 and contained the H_2-TPR studies with formation of H_2O. These studies suggest the reaction mechanism proceeding via formation of formate intermediate, with the decomposition temperature for surface formate to be lower for Rh/CeO_2 compared to bare ceria. The surface formate species were observed to be present as bidentate formate with the addition of CO at 500 K. The study also indicates the possibility of bidendate carbonate with two coordination sites suggesting a dual site mechanism to be operational.

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