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# Pd and Pt ions as highly active sites for the water–gas shift reaction over combustion synthesized zirconia and zirconia-modified ceria

Parag A. Deshpande [a], M.S. Hegde [b], Giridhar Madras [a,b,*]

[a] Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India
[b] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Noble metal substituted ionic catalysts were synthesized by solution combustion technique. The compounds were characterized by X-ray diffraction, FT-Raman spectroscopy, and X-ray photoelectron spectroscopy. Zirconia supported compounds crystallized in tetragonal phase. The solid solutions of ceria with zirconia crystallized in fluorite structure. The noble metals were substituted in ionic form. The water–gas shift reaction was carried out over the catalysts. Negligible conversions were observed with unsubstituted compounds. The substitution of a noble metal ion was found to enhance the reaction rate. Equilibrium conversion was obtained below 250 °C in the presence of Pt ion substituted compounds. The formation of Bronsted acid–Bronsted base pairs was proposed to explain the activity of zirconia catalysts. The effect of oxide ion vacancies on the reactions over substituted ceria–zirconia solid solutions was established.

## 1. Introduction

Synthesis of solids for applications in catalysis should impart some important characteristics to the solids. Mechanical properties like surface area, porosity, thermal and mechanical stability and surface characteristics have been identified as important parameters influencing the catalyst performance [1]. Therefore, the development of methods of the synthesis, which can restrict the crystallite size to nanometer dimensions, is of interest. Nanocrystalline solids provide high surface area, high surface accessibility, and ease of regeneration in case of carbon deposition or coking. The nanoscale dimensions and the shapes of the solids have been reported to influence the catalyst performance. Si and Flytzani-Stephanopoulos [2] have shown high shape dependence of CO conversion over Au–$CeO_2$ for the water–gas shift reaction (WGS). Zhau et al. [3] have shown higher activity of $CeO_2$ nanoflowers as compared to nanocubes and nanopolyhedra for CO oxidation.

Several investigators have shown the morphological effects of the solids on the catalytic properties [4–5]. High thermal stability has been observed by Crepaldi et al. [6] for the three-way catalysis in case of nanocrystalline ceria–zirconia thin films, and by Wang et al. [7] for ceria nanopowders. Kleinlogel and Gauckler [8] have shown that nanosized solid solutions of ceria with gadolinium added with suitable transition metals show size dependent sintering behavior, which render them suitable for use as catalytic electrodes. Therefore, it is desirable to synthesize solids for catalytic application by methods which can limit the crystallite size to nanometer range and impart good catalytic properties. The solution combustion technique is one of such methods. With this technique, solids with high specific surface and crystallite size in nanometer range can be obtained [9–11]. In this study, we have synthesized noble metal substituted nanosized zirconia and ceria–zirconia solid solutions by solution combustion technique and have carried out WGS over these materials.

WGS has been studied on supported catalysts involving zirconia and ceria–zirconia by several investigators. $ZrO_2$ supported Pt and Au compounds have been reported to catalyze WGS [12–19]. According to Boaro et al. [13], $ZrO_2$ exhibits polymorphism. This phenomenon provides different sites for the catalysis and makes it a suitable support. Although $ZrO_2$ is not easily reducible by $H_2$, its reducibility can be enhanced by introduction of Pt [20]. Since WGS involves oxidation of CO to $CO_2$ it may involve the corresponding reduction of the support and it becomes desirable to have a reducible support material. The introduction of Pt in $ZrO_2$ enhances the reducibility of the support and, therefore, Pt substituted $ZrO_2$ is expected to act as a good catalytic material for the WGS reaction.

According to Tibiletti et al. [12], noble metals supported over pure oxides like $ZrO_2$ or $CeO_2$ show lower activity as compared to

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[*] Corresponding author. Tel.: +91 80 2293 2321; fax: +91 80 2360 0683.
*E-mail addresses:* giridhar@chemeng.iisc.ernet.in, giridharmadras@gmail.com (G. Madras).

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the corresponding mixed oxides. $ZrO_2$ has a poor reducibility as compared to $CeO_2$. However, the reducibility of $CeO_2$ can be enhanced by the introduction of $ZrO_2$. This has been proved experimentally as well as by DFT calculations [21–23]. Therefore, much attention has been focused towards the use of mixed oxides and solid solutions of $CeO_2$–$ZrO_2$. Such oxides have shown high activity towards gas phase oxidation reactions [24–27].

The catalytic activity of the solids has been reported to be greatly influenced by the preparation method [13,18–19,28]. The properties like crystallinity, crystal size, and surface area are dependent on the method of preparation. The solution combustion method is a novel technique for the synthesis of nanocrystalline catalytic compounds. We have previously reported the catalytic activity of noble metal substituted $CeO_2$ for exhaust catalytic applications [11]. In this study, we show the activity of the catalysts for WGS. The use of noble metal ion substitution for $Zr^{4+}$ and $Ce^{4+}$ in $ZrO_2$ and $CeO_2$–$ZrO_2$ solid solutions for WGS is not reported in the literature. This study provides an insight into the mechanism of WGS on the basis of the catalyst structure and the various experimental observations.

## 2. Experimental

### 2.1. Chemicals and instruments

Zirconium nitrate ($Zr(NO_3)_4{\cdot}5H_2O$, Loba Chemie, India), ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$, Loba Chemie, India), palladium chloride ($PdCl_2$, Loba Chemie, India), tetraammine platinum (II) nitrate ($(NH_3)_4Pt(NO_3)_2$, Sigma–Aldrich, USA) and oxalyldihydrazide ($C_2H_6N_4O_2$, Alfa Aesar, India) were used for the synthesis of the compounds. CO (10.33% in $N_2$, Chemix Speciality Gases, Bangalore, India), and ultrahigh purity $H_2$, $CO_2$ and $N_2$ (all from Vinayaka Gases, Bangalore, India) were used for the catalytic reactions.

The powder X-ray diffraction patterns (XRD) were recorded on Phillips X'pert diffractometer using CuKα radiations. The scan rate and $2\theta$ range were fixed at 0.067 °/min and 5–90°, respectively, for all the scans. The X-ray photoelectron spectra (XPS) were recorded on Thermo Fisher Scientific Multilab 2000 (England) instrument with AlKα radiations (1486.8 eV). The FT-Raman spectra were recorded on NXR-FT Raman module (Thermo Scientific, USA) equipped with Ge detector and Nd:$YVO_4$ laser. An online gas chromatograph (Nano HP-I, Mayura Analyticals Pvt. Ltd., Bangalore, India) was used for the analysis of the product gas mixture during the catalytic reactions.

### 2.2. Catalyst synthesis

The compounds were synthesized using the solution combustion technique. The technique involves the combustion of a salt of the support and a noble metal salt with a fuel in a solution. Zirconium nitrate, Pd or Pt salt and oxalyldihydrazide (as a fuel) were taken in a molar ratio of 0.98:0.02:1.96. The chemicals were mixed in a crystallizing dish. A small amount of water was added to make the solution. A few drops of nitric acid were added to obtain a clear solution. The solution was heated in a preheated muffle furnace at 350 °C. The solution underwent a spontaneous combustion to yield noble metal substituted zirconia that could be represented by the formula $Zr_{0.98}M_{0.02}O_2$ (M = Pd or Pt). For the synthesis of ceria–zirconia solid solutions, ceric ammonium nitrate, zirconium nitrate, Pd or Pt salt and oxalyldihydrazide were taken in a molar ratio of 0.83:0.15:0.02:2.4 and the combustion steps were repeated. The product obtained could be represented by the formula $Ce_{0.83}Zr_{0.15}M_{0.02}O_{2-\delta}$. The porous combustion products thus obtained were finely ground and heated at 500 °C for 24 h.

### 2.3. Catalytic reactions

WGS was carried out over the above synthesized catalysts. The reactions were carried out with 2% CO concentration (by volume). A total flow rate of 100 ml/min was maintained. This corresponded to a dry space velocity of 95,000 $h^{-1}$. The reaction was carried out in a quartz tube reactor of 4 mm i.d. The catalysts were made into granules of 150–300 μm and packed between ceramic wool. A thermocouple was used for measuring the bed temperature. The thermocouple was dipped in the catalyst bed. The reactors were heated from outside using an electric heater. The temperature was regulated using a PID controller. The reactant gas mixture was sent through flow controllers to maintain a dry gas flow rate of 100 ml/min. Water was pumped using an HPLC pump. A constant water flow of 0.1 ml/min was maintained. The line used for supplying water till the reactor was heated using an external heating tape. The temperature of the line was maintained at 150 °C using a temperature controller to keep the water in vapour phase and avoid its condensation. Idakiev et al. [19] have studied the influence of $H_2O$/CO ratio on CO conversion. It was found that at a given temperature, the increase in $H_2O$ has an effect over the % CO conversion only at very small $H_2O$/CO ratio ($<10$). At higher $H_2O$ concentrations, the conversions remain independent of $H_2O$ concentration. Therefore, the kinetics of reaction becomes independent of $H_2O$ concentration. However, with an increase in $H_2O$ concentration, the equilibrium shifts towards the forward direction. Therefore, high $H_2O$ concentrations were used. The water line was joined with the gas line and the lines were heated to avoid the condensation of water. The unreacted water was condensed using a condenser dipped in an ice cold water bath. The dry product gas mixture was sent to an online gas-chromatograph unit (HP-Nano *I*, Mayura Analyticals Pvt. Ltd., Bangalore, India). A single step separation of all the gases in the mixture was done using Hayesep-A and molecular sieve columns. Flame ionization detector and thermal conductivity detectors were used for detection of all the components of the gas mixture.

## 3. Results and discussion

### 3.1. Structural analysis

The crystal structure of the synthesized compounds was determined by XRD and was confirmed by FT-Raman spectroscopy. For finding the structural parameters, the XRD data were Rietveld refined using the FullProf suite program 1.0 [29]. The algorithm utilizing the non-linear least square fit was used to compare the observed peak intensities against the theoretically calculated intensities. The symbols in the figures show the experimental XRD data, the solid lines show the predicted XRD pattern. The difference between the actual and theoretical pattern is shown by the light line at the bottom. Fig. 1 shows the Rietveld refined XRD pattern of as prepared $ZrO_2$. The diffraction lines could be indexed to the tetragonal phase of zirconia. Fitting of the data to the tetragonal structure gave satisfactory values of the reliability data. Table 1 shows the cell parameters, crystallite size and the refinement reliability data for all the compounds. The fitting of the pattern to the monoclinic and the cubic structure gave poor fitting parameters. Small peaks around 28°, 29° and 32° were observed in the XRD of all the $ZrO_2$ compounds. Fig. 2 shows the extended XRD of $ZrO_2$ compounds in a small $2\theta$ range of 27–33°. The characteristic monoclinic lines appear in this region. Diffraction lines at 28.5°, 29° and 31.5° (marked by asterisks) could be observed. This showed the crystallization of a small amount of $ZrO_2$ in monoclinic phase.

The XRD spectra of the compounds were recorded both before and after the reaction to observe the changes in the crystal