

Effect Of Morphological Characteristics Of Supported Platinum Catalysts On Their Activity For The Water Gas Shift Reaction

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1. Introduction

The Water Gas Shift (WGS) reaction has become attractive during the last decades due to its potential use in fuel processors for mobile and small-to-medium size stationary fuel cell systems. In such applications the WGS can be used for the production of additional hydrogen and the elimination of CO contained in syngas produced via catalytic reforming of carbon containing compounds. The WGS reaction is exothermic and equilibrium limited and therefore, two WGS reactors are typically used in industry. One operating at high temperatures (HT) for rapid CO conversion, and a second one operating at low temperatures (LT) in order to achieve the desired low CO levels. However, the conventional HT (Fe-Cr) and LT (Cu-Zn) WGS catalysts cannot be used for Polymer Electrolyte Membrane full cell applications operating in the temperature range of 200-280 °C mainly due to restrictions in volume, weight and cost. [1]. Noble metal based catalysts were found to be able to meet the above criteria and, therefore, have been widely studied with Pt/CeO₂ catalysts being among those exhibiting exceptionally high WGS activity at low reaction temperatures [2]. The main disadvantage of Pt/CeO₂ catalysts is their tendency to deactivate under typical conditions of reformer's outlet. Therefore, the optimization of such catalyst formulations requires special attention in order to develop active WGS catalysts with improved life time. In the present study, the catalytic performance of Pt (0.5 wt.%) supported on CeO₂ and Gadolinium-Doped-Ceria (GDC) carriers prepared employing two different methods leading to carriers with different morphological characteristics was investigated for the WGS reaction. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was also performed in order to identify the active sites and reaction intermediates involved in the reaction pathway.

2. Experimental

Ceria and GDC supports were synthesized employing the hydrothermal and precipitation methods. Dispersed Pt (0.5 wt.%) catalysts were prepared by the wet impregnation method with the use of the aforementioned supports and an aqueous solution of (NH₃)₂Pt(NO₂)₂ as the metal precursor salt. Platinum catalysts supported on commercial CeO₂ and GDC powders were also synthesized for comparison purposes. Catalysts were characterized employing nitrogen physisorption at -196 °C, X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and H₂-Temperature Programmed Reduction (H₂-TPR) experiments. Catalytic performance tests were carried out in the temperature range of 250-650 °C using 100 mg of catalyst, a total flow rate of 150 cm³/min and a feed composition consisting of 10%H₂ + 10%CO + 5%CO₂ + 35%H₂O/Ar. The reaction mechanism was investigated employing DRIFTS studies in the temperature range of 25-500 °C using a gas stream consisting of 1%CO + 3.5%H₂O.

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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης

3. Results and Discussion

TEM measurements (not shown here) revealed that CeO₂ and GDC carriers synthesized by the hydrothermal method led to the development of oxides with nanorods structure (denoted in the following as CeO_{2nanorods} and GDC_{nanorods}) whereas the precipitation method resulted in the formation of CeO₂ and GDC with spherical nanoparticles (denoted in the following as CeO_{2spherical} and GDC_{spherical}). The H₂-TPR profiles obtained from the preoxidized Pt catalysts supported on the synthesized CeO₂ and GDC samples are characterized by two hydrogen consumption features: a low temperature (LT) peak, with its maximum located below 200 °C, and a high temperature (HT) feature, which evolves above 300 °C. The LT peak is attributed to the reduction of PtO_x species and the HT peak to the reduction of the support which is in close contact with Pt particles. It was observed that the LT peak appears at lower temperatures for the samples with nanorods structure compared to those with spherical particles. In the case of Pt/CeO₂ catalysts the HT peak appears at lower temperatures when Pt is supported on CeO_{2nanorods} than on CeO_{2spherical}, whereas in the case of Pt/GDC catalysts the HT peak can only be discerned when GDC_{nanorods} is used as catalyst support. Results indicate that the nanorods structure of CeO₂ or GDC favors the reduction of both PtO_x species and support's surface.

Results of catalytic performance experiments are presented in Fig.1A, where the conversion of CO has been plotted as a function of reaction temperature and compared with the equilibrium conversion predicted by thermodynamics (dashed line). It is observed that Pt catalysts dispersed on GDC with nanorods structure exhibit higher CO conversions compared to those supported on CeO₂ of the same structure especially at high reaction temperatures. This is also the case when commercial oxide powders are used as supports, whereas Pt/GDC_{spherical} and Pt/CeO_{2spherical} catalysts present identical performance. Optimum results were obtained for Pt/GDC_{nanorods} which is activated above 250 °C and reaches the equilibrium conversion curve at 480 °C and is much more active than those dispersed on commercial supports. It can be observed that the nanorods structure of the support exhibits significantly improved performance compared to the spherical structure independently on whether CeO₂ or GDC is used as support. This can be correlated with the improved reducibility found for supports with nanorods structure and agrees well with previous studies where it has been reported that the WGS activity increases with increasing the reducibility of the support [1]. The intrinsic reaction rate presented in an Arrhenius type diagram of Fig.1B depends strongly on the type of the support employed and increases by a factor of 5 following the order Pt/GDC_{spherical}~Pt/CeO_{2spherical} < Pt/CeO_{2commercial} < Pt/GDC_{commercial} < Pt/CeO_{2nanorods} < Pt/GDC_{nanorods}. The stability of Pt/GDC_{nanorods} was also investigated and results implied that it presents excellent stability for about 30 hours on stream.

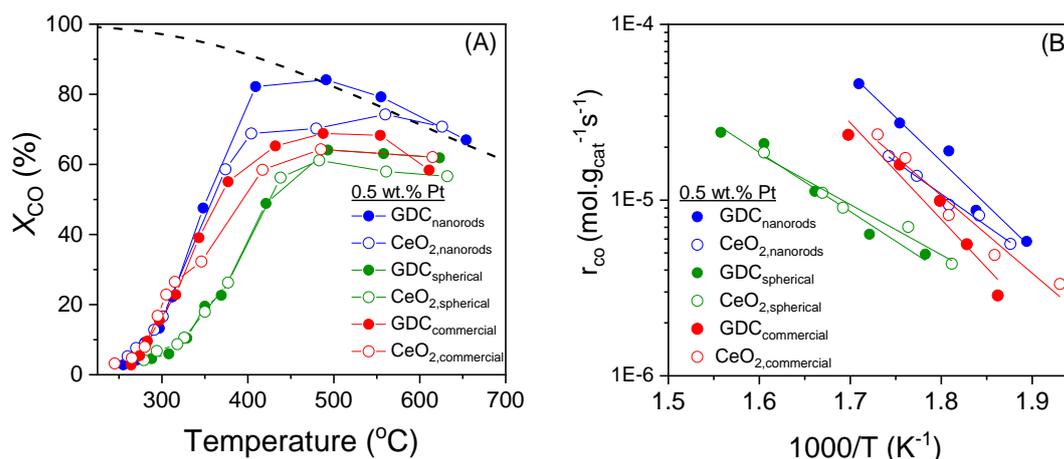


Figure 1. Effect of the nature and morphology of the support on (A) the CO conversion and (B) the intrinsic reaction rate of Pt catalysts for the WGS reaction.

The WGS reaction was also investigated employing *in situ* FTIR spectroscopy. Representative results obtained from Pt/GDC_{nanorods} and Pt/GDC_{spherical} catalysts following their interaction with

1%CO+3.5%H₂O (in He) mixture at 25 °C for 15 min and subsequent stepwise heating up to 500 °C are shown in Fig.2. It is observed that Pt/GDC_{nanorods} exposure to reaction mixture at 25 °C leads to the development of several bands assigned to formate and/or carbonate species associated with the support (<1700 cm⁻¹), three bands in the ν(CO) stretching frequency region previously assigned to CO linearly adsorbed on partially oxidized (2084 cm⁻¹) and reduced (2061 cm⁻¹) platinum sites, and bridged-bonded CO (1825 cm⁻¹), and two negative bands (3665, 3633 cm⁻¹) assigned to two types of different surface OH groups (Fig.2A). Progressive increase of temperature results in the development of new bands located at 1583, 1372, 2945, 2838 and 2704 cm⁻¹ which are due to formate species adsorbed on GDC surface [2,3]. An additional band located at 1969 cm⁻¹ can be also discerned in the spectrum recorded at 250 °C which based on previous studies can be attributed to CO adsorption at Pt–Ce³⁺ sites located at the metal/support interface [2,3]. It can then be suggested that the WGS reaction proceeds via the associative mechanism according to which CO adsorbed on platinum interacts with hydroxyl groups of CeO₂ at the metal/support interface producing formate species which are eventually decomposed to CO₂ and H₂. In the case of Pt/GDC_{spherical} catalysts no bands assigned to formate species and CO adsorbed at the metal-support interface can be observed (Fig.2B) indicating that either this catalyst follows a different reaction pathway or the population of the aforementioned bands is too low that cannot be discerned in the obtained spectra resulting in low WGS reaction rate.

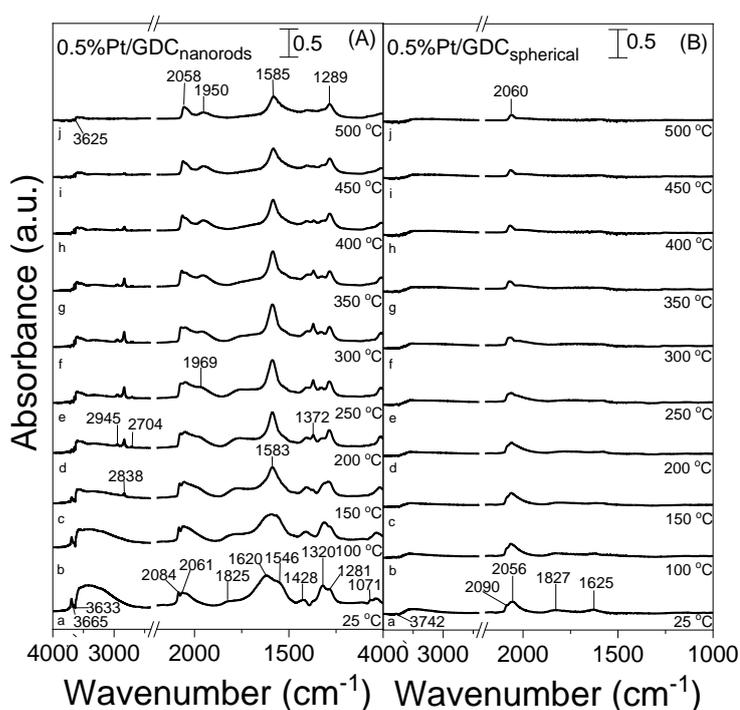


Figure 2. DRIFT spectra obtained from (A) 0.5%Pt/GDC_{nanorods} and (B) 0.5%Pt/GDC_{spherical} catalysts following interaction with 1%CO+3.5%H₂O at 25°C and stepwise heating at 500 °C.

4. Conclusions

Results of the present study showed that the WGS activity depends strongly on both the nature and morphological characteristics of the support. The reducibility of both PtO_x species and the support is enhanced when GDC or CeO₂ is characterized by nanorods structure. Among the investigated catalyst Pt/GDC_{nanorods} was found to exhibit superior activity and excellent stability for 30 hours on stream. Results of DRIFTS studies provide evidences that the WGS reaction proceeds via the associative mechanism with the metal-support interface providing the active sites for CO activation and conversion toward the reaction products.

References

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