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The effect of La^{3+}, Ti^{4+} and Zr^{4+} dopants on the mechanism of WGS on ceria-doped supported Pt catalysts

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Platinum nanoparticles supported on single CeO_2 and TiO_2 metal oxides and $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ solid solution were prepared to investigate the effect of Ti^{4+}-doping of ceria on important mechanistic and kinetic aspects of the Water–Gas Shift (WGS) reaction in the 200–300 °C range, namely: (i) the concentration and chemical structure of active adsorbed reaction intermediates present in the C-path and H-path of WGS, and (ii) the prevailing mechanistic path among "redox" and "associative" both proposed in the literature. The relationship between the chemical nature of dopant (Zr^{4+}, Ti^{4+} and La^{3+}) and the concentration of active C-pool and H-pool of reaction intermediates as well as that of specific rate per gram basis (r_{CO}, $\mu mol\,g^{-1}\,s^{-1}$) for the ceria-doped supported Pt is illustrated for the first time based on relevant results previously reported (Zr^{4+} and La^{3+}-doped ceria). The 0.5 wt% Pt supported on $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ (Ti^{4+}-doped CeO_2) exhibits significantly higher WGS activity in terms of CO conversion (%) and specific kinetic rate ($\mu mol\,CO\,g^{-1}\,s^{-1}$ or $\mu mol\,CO\,cm^{-1}\,s^{-1}$) compared to Pt/$CeO_2$, Pt/$TiO_2$, Pt/$Ce_{0.8}La_{0.2}O_{2-\delta}$ and Pt/$Ce_{0.5}Zr_{0.5}O_{2-\delta}$ catalysts. This was explained mainly by: (i) the larger concentration of active C-pool of reaction intermediates formed around each Pt nanoparticle, and (ii) the higher reactivity of sites (k, s^{-1}) along the Pt-support interface responsible for CO_2 and H_2 formation. A very good correlation between the concentration of *active* C-pool and the *specific reaction rate*, r_{CO} ($\mu mol\,g^{-1}\,s^{-1}$) as a function of the dopant (Zr^{4+}, La^{3+} and Ti^{4+}) was found. The concentration of labile surface oxygen and its mobility in $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ compared to CeO_2 (undoped), La^{3+} or Zr^{4+}-doped ceria are also important factors. It is proposed that on Pt/CeO_2-doped catalysts the WGS reaction follows both the "redox" and "associative formate" mechanisms, where the extent of participation of each mechanism depends on the chemical nature of the dopant (Zr^{4+}, La^{3+} and Ti^{4+}).

1. Introduction

The heterogeneously catalyzed Water–Gas Shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta H^\circ = -41.2$ kJ/mol) is one of the key steps in fuel processing systems and in a number of chemical processes, including steam reforming of hydrocarbons, sugars, alcohols and bio-oil for hydrogen production, and the manufacturing of ammonia and petroleum refinery products [1–5].

The low-temperature Water–Gas Shift (LTS) industrial catalyst ($Cu/ZnO/Al_2O_3$) is pyrophoric, and deactivates if exposed to air and condensed water, and it is characterized by low thermal stability [6]. Recently, attempts have been focused towards the development of low-loading robust noble metal-based catalysts with high activity at low-temperatures, and which are non-pyrophoric, in order to reduce catalyst volume and cost [4]. Supported Pt metal catalysts on reducible metal oxide carriers appear to be promising candidates for replacing current industrial low-temperature WGS catalysts [5]. CeO_2 [4,7–13], TiO_2 [14–16], La_2O_3 [17–20] and ZrO_2 [9–11,21,22] as single or mixed metal oxides have been investigated. However, the stability of these catalytic systems under practical WGS reaction conditions remains one of the problems that need to be solved.

It is generally accepted that the WGS reaction over metal oxide-supported noble metal catalysts operates in a bifunctional manner with the participation of both the dispersed metal phase and the support. Two general mechanistic schemes have been proposed: (i) the "redox or regenerative" mechanism [14,23–27], and (ii) the "adsorptive or associative" mechanism [12–14,28–30]. However, several important kinetic and mechanistic aspects of the WGS over supported metal catalysts still remain controversial, namely: the dominant mechanistic path, the rate-determining step, the chemical nature of the *active* "carbon-containing" and "hydrogen-containing" intermediates, and their true site location (e.g. support, metal-support interface, metal surface or metal and

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support surfaces) [12,31–35]. Therefore, the fundamental understanding of the WGS reaction at the molecular level is of paramount importance in order to design proper functional catalytic materials for activity, selectivity and stability optimization under industrial WGS reaction conditions. Towards the achievement of this goal, mechanistic aspects of the WGS reaction using in situ spectroscopic and kinetic measurements under reaction conditions (*operando* methodology) are highly desirable [12–14,20,33,36].

The present work reports on the effects of ceria doping with Ti^{4+} cations on the catalytic behaviour and important kinetic and mechanistic aspects of the WGS in the low-temperature range of 200–325 °C over Ti^{4+}-doped ceria-supported Pt. This work is a continuation of previous ones [20,36], where the effect of doping of ceria with La^{3+} [20] and Zr^{4+} [36] cations was reported. In the present work it is demonstrated how the concentration (μmol g^{-1}) of the *active* C-pool and H-pool, and the extent (Δx, nm) of a reactive zone formed around each Pt nanoparticle are influenced by the presence of Zr^{4+}, La^{3+} or Ti^{4+} cation dopant in the ceria support matrix. Also, correlations between the *active* C-pool and H-pool and the specific WGS reaction rate as a function of dopant (Zr^{4+}, La^{3+} and Ti^{4+}) are probed. To our knowledge, this is the first time that such relationships are derived for the WGS reaction on ceria-doped supported Pt catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ solid solution (Ti^{4+}-doped CeO_2) and the single metal oxides of CeO_2 and TiO_2 used as supports of Pt (0.5 wt%) were synthesized using a modified citrate sol–gel technique described in detail elsewhere [20]. The supported Pt catalysts were prepared by impregnating the oxidic supports with a given amount of diluted aqueous solution of H_2PtCl_6 (8 wt% solution in water, Aldrich) so as to yield a 0.5 wt% Pt nominal loading. Prior to catalytic measurements, the fresh catalyst sample was in situ pretreated in 20 vol% O_2/He (50 N mL min^{-1}) gas mixture at 600 °C for 2 h followed by reduction in H_2 (1 bar, 50 N mL min^{-1}) at 300 °C for 2 h.

Platinum particle size distribution and a mean Pt particle size (d_{Pt}, nm) for the 0.5 wt% Pt/CeO_2, 0.5 wt% Pt/TiO_2 and 0.5 wt% Pt/$Ce_{0.8}Ti_{0.2}O_{2-\delta}$ catalysts were directly determined by High Angle Annular Dark Field (HAADF) images obtained using a 200 kV JEM-2100J (Jeol Ltd) transmission electron microscope [20]. Platinum dispersion was estimated after considering the relationship: $D\,(\%) = 1.1/d_{Pt}\,(\text{nm}) \times 100$.

2.2. Steady-state WGS reaction

Steady-state WGS catalytic measurements were conducted in the experimental set-up previously described [37]. The reaction feed composition used consisted of 3 vol% CO/10 vol% H_2O/He, and the total volume flow rate was 200 N mL min^{-1}, resulting in a GHSV of about 40,000 h^{-1} (L/L_{cat}/h). The powder catalyst's particle size was between 0.1 and 0.2 mm, and the amount of catalyst sample used was 0.5 g. The catalytic performance of Pt/$Ce_{1-x}Ti_xO_{2-\delta}$ (x = 0.0, 0.2 and 1.0) solids in terms of X_{CO} (%) versus the reaction temperature was evaluated in the 200–325 °C range over an in situ pre-reduced catalyst in H_2 flow (1 bar, 50 N mL min^{-1}) at 300 °C for 2 h. The effluent gas stream from the micro-reactor after removing the water (Peltier Gas Cooler, model ECP1000, M&C TechGroup) was directed to a mass spectrometer (Omnistar, Balzer) for on line monitoring the H_2, CO and CO_2 gas composition. The purity of H_2, He, CO, and Ar gases (Linde Gas, Greece) was higher than 99.95%.

2.3. SSITKA-mass spectrometry studies

The SSITKA-MS experiment performed to follow the hydrogen-path of the WGS reaction involved the switch 3 vol% CO/10 vol% H_2O/Ar/Kr (T, 30 min) → 3 vol% CO/10 vol% D_2O/Ar (T, t), whereas that to follow the carbon-path of WGS involved the switch 3 vol% ^{12}CO/10 vol% H_2O/Ar/He (T, 30 min) → 3 vol% ^{13}CO/10 vol% H_2O/Ar (T, t). The effluent wet gas stream from the reactor was first passed through a condenser (Peltier system of low volume), the exit of which was directed to a mass spectrometer for *on line* monitoring the normal and isotope-containing (D, ^{13}C) reactants and products composition (e.g. H_2, HD, D_2, ^{12}CO, ^{13}CO, $^{12}CO_2$ and $^{13}CO_2$). The isotopes used in the SSITKA experiments were ^{13}CO (99.9 atom% ^{13}C, Spectra Gases) and deuterium oxide (D_2O, 99.96 atom% D, Aldrich). The mass of the catalyst was adjusted in every SSITKA-MS experiment so as to keep the CO conversion below 15%; the total mass of catalytic bed was 0.5 g (catalyst + SiO_2 for dilution when needed). More details on the SSITKA-MS experiments and the micro-reactor used were previously reported [12,20,36,38–40].

2.4. Probing the H-exchange between —OH groups of support and D_2O or D_2 gases

In order to account for possible H-exchange between the —OH groups of support and the D_2O(g) and D_2(g) during the SSITKA-MS experiment at 300 °C for measuring the active H-pool, the following experiments were performed:

(a) The catalyst sample was first treated in 10 vol% H_2O/Ar (100 N mL min^{-1}) at 300 °C for 30 min, and then the feed was switched to an equivalent mixture of 10 vol% D_2O/Ar, and the transient evolution of HD, H_2 and D_2 gases at the latter switch was followed with time on stream by mass spectrometry.

(b) The catalyst sample was first treated with 10 vol% H_2O/Ar (100 N mL min^{-1}, 30 min) at 300 °C followed by an Ar (100 N mL min^{-1}) purge at 300 °C for 10 min. The feed was then switched to an x vol% D_2/Ar gas (100 N mL min^{-1}), and the transient evolution of HD and H_2 gases was followed with time on stream. The x vol% composition of D_2 was chosen to be the same as that achieved in 3 vol% CO/10 vol% D_2O/He gas treatment under steady-state WGS reaction conditions at 300 °C.

2.5. SSITKA-DRIFTS studies

SSITKA-DRIFTS experiments with ^{13}CO (99.9 atom% ^{13}C, Spectra Gases) involved the switch 3 vol% ^{12}CO/10 vol% H_2O/Ar/He (T, 30 min) → 3 vol% ^{13}CO/10 vol% H_2O/Ar (T, t) at a total flow rate of 200 N mL min^{-1} which potentially allows determining the chemical structure of the *active* intermediates and *spectator* species of the WGS reaction. All the SSITKA-DRIFTS experiments were performed in a specially designed gas flow-system described in detail elsewhere [39]. Signal averaging was set to 128 scans per spectrum (averaged), and the spectra were collected in the 4000–500 cm^{-1} range at the rate of 0.2 s/scan (MCT detector), and using a resolution of 4 cm^{-1}. The background spectrum of the solid was taken under 10 vol% H_2O/Ar flow at the desired reaction temperature. After background subtraction, a baseline correction was performed according to the provided software (PerkinElmer Spectrum, v.10.03.02). More details on the SSITKA-DRIFTS experiments and the DRIFTS reactor cell used were reported [12,14,20,36,39,40].

2.6. Probing CO_2 readsorption effects and rival WGS reaction mechanisms

The initial rate of reaction of adsorbed formate and CO with water alone was measured by a novel experiment recently