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Short communication

Effect of nanostructured support on the WGSR activity of Pt/CeO_2 catalysts

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ABSTRACT

The water gas shift catalytic activity and methane selectivity of Pt/CeO_2 catalysts are shown to be strongly dependent on the platinum–ceria interaction. Platinum nanoparticles supported on nanostructured ceria rods present a higher hydrogen yield and lower methane selectivity than its counterpart catalysts supported on ceria nanoparticles or nanocubes, despite the similitude in platinum particle size. Indeed, the constraints of the 1D crystal structure of the ceria nanorods and the selective exposure of the (110) crystal plane are directly related to its superior catalytic activity. Platinum nanoparticles do not only act as active sites for CO adsorption and oxidation but also affect the reducibility of the support.

1. Introduction

Hydrogen is widely recognised as a key component in our current search for a renewable and sustainable energy sector. Its conversion in fuel cells in both mobile and stationary applications can provide clean and efficient transportation fuel and electricity. However, highly-pure hydrogen is required as feedstock for fuel cells to avoid the poisoning of the electrodes and its consequent irreversible loss of activity [1]. In the last decade, there has been significant increase in interest in the water gas shift reaction (WGSR) for the production of CO-free hydrogen at temperatures (100–180 °C) relevant to the fuel cell technology [2,3]. Hydrogen produced by the reforming of hydrogen-rich fuels such as natural gas, methanol or gasoline can contain up to ~10–15% carbon monoxide [4,5], and the WGSR is presented as a pathway for its removal while increasing the overall hydrogen yield.

Conventional commercial low temperature shift catalysts based on $Cu/ZnO/Al_2O_3$ materials [6] present insurmountable limitations, namely low activity at the relevant fuel cell temperature range, pyrophoric nature and weak stability under cyclic operation. Alternatively, noble metals (Pt, Au, Pd) supported on reducible oxides such as CeO_2 or TiO_2 have been widely presented as highly active and stable WGSR catalysts [7–9]. The reducibility of the surface oxygen of ceria was long ago discovered to be greatly promoted by the addition of platinum to its surface [10] with a consequent enhancement of its WGSR activity. Flytzani-Stephanopoulos's group more recently demonstrated that the active sites for the WGSR are platinum species diffused in the subsurface layers of ceria [11], which weaken the surface Ce–O bond, making this oxygen reactive at lower temperatures [12,13]. The mechanism of formation of these active Pt–Ce–O active species seems to strongly depend on the preparation method as well as being highly sensitive to the ceria structure, even when the metal crystallite size remains constant [14]. Furthermore, addition of dopants into the ceria have been demonstrated to modify the Pt-support interaction and consequently the resulting WGSR activity, having a direct effect on the reaction mechanism [15,16]. We have recently demonstrated that the oxygen storage capacity and low temperature reducibility of the ceria can be tuned by varying its morphology at the nano-scale by selectively exposing different crystal planes [17], leading to further studies by other groups [18,19]. In this paper, we demonstrate the relationship between the surface chemical and physical properties of nanostructured ceria and the resulting platinum-support interaction, reducibility of ceria and consequently, WGSR activity, providing relevant insights for future catalyst design in this field.

2. Experimental

Nanostructured ceria with different nano-morphologies were selectively synthesised by varying the conditions during hydrothermal treatment using $Ce(NO_3)_3{}^\circ 6H_2O$ as a precursor [17]. Ceria nanorods were synthesised at 100 °C in a 15 M NaOH solution while ceria nanocubes were formed at 180 °C in a 15 M NaOH medium as described elsewhere

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[20]. Commercial ceria nanoparticles (Sigma) were also used for comparison purposes. Platinum was supported by incipient wetness impregnation at room temperature using a commercial 8% H_2PtCl_6 aqueous solution (pH = 3) as a metal precursor. Catalysts were dried under vacuum at 80 °C and reduced during 2 h under 20 mL/min hydrogen flow at 200 °C.

N_2 adsorption analysis at 77 K were carried out using a Micromeritics ASAP 2020. The morphology of the ceria materials and the platinum nanoparticle size distribution was determined with a JEOL TEM-2100 200 kV transmission electron microscope. CO pulse chemisorption analyses at 35 °C were carried out using a Micromeritics Autochem II equipment equipped with a thermal conductivity detector (TCD) after sample reduction under hydrogen flow at 200 °C followed by a pre-treatment at 300 °C under helium flow. The same equipment was used for the temperature programmed reduction experiments using 5% H_2/Ar with a ramp rate of 10 °C min^{-1}. The first TPR cycle was performed without any prior-treatment of the sample while 20 mL/min of helium were flown at room temperature during 10 min between consecutive temperature programmed experiments.

The water gas shift reaction catalytic activity of the nanostructured 1.5%Pt/CeO_2 catalysts was studied in a differential fixed-bed reactor at atmospheric pressure where 35 mg of catalyst were diluted in SiC to a total 4 cm^3 volume and packed into a 6 mm ID ceramic tube. The reactant gas mixture (100 mL min^{-1}) consisted of Ar (90%), CO (5%) and H_2O vapour (5%) with a GHSV of 4520 h^{-1}. The outlet reaction stream was analysed by on-line gas chromatography equipped with a TCD detector (Varian-3900). Each analysis was repeated three times with an associated experimental error < 5%.

3. Results and discussion

Three nanostructured ceria materials (nanorods, nanocubes and nanoparticles) with different physical properties were used in a series of Pt/CeO_2 catalysts. In all cases, the platinum amount was fixed to 1.5 wt.%, loaded by wetness impregnation. Ceria nanorods present diameters of ~7 nm and lengths in the range of 20–80 nm and a surface area of 74 $m^2\ g^{-1}$, enclosing (110) and (100) facets. Ceria nanocubes present bigger dimensions, with sizes from 20 to 100 nm and relatively small surface area (13 $m^2\ g^{-1}$), enclosing (100) facets. Ceria nanoparticles have the highest surface area amongst the materials studied here (144 $m^2\ g^{-1}$) with dimensions ~ 5 nm, enclosing (111) and (100) facets. Full physical characterisation of these materials is published elsewhere [17].

The activity of the different Pt/CeO_2 catalysts for the WGSR as a function of temperature is shown in Fig. 1A. Carbon monoxide conversion increases as the temperature increases, reaching a plateau (or even decreasing in the case of the 1.5wt.%Pt/CeO_2 rods) at high reaction temperatures due to thermodynamic limitations.

The 1.5 wt.% Pt/CeO_2 rods catalyst presents not only higher activity with respect to the 1.5 wt.% Pt/CeO_2 cubes and 1.5 wt.% Pt/CeO_2 particles, but also reactivity at considerable lower temperatures (180 °C). It is important to highlight that lowering the reaction temperature has a direct impact on the energy efficiency and yield of the final hydrogen production process and CO removal application. The 1.5 wt.% Pt/CeO_2 cubes and 1.5 wt.% Pt/CeO_2 particles present water gas shift activity at temperatures >225 °C with the latter showing a slightly higher activity within the studied temperature range. Comparison of these catalysts to those reported in the literature proved to be difficult due to the variations on the experimental conditions amongst studies, specifically the inlet H_2O/CO ratio which affects not only the thermodynamic equilibrium but also the rate of re-oxidation of ceria.

Fig. 2 shows representative TEM images of the Pt/CeO_2 catalysts. None of the ceria materials undergo morphological transformation upon the loading of the platinum or their reduction showing the same morphology and dimensions than the fresh ceria materials [17]. The three catalysts present platinum nanoparticles with sizes < 2 nm, some of them indicated by arrows in Fig. 2, without the presence of metal agglomerations. No accurate particle size distributions were achieved due to the small platinum size.

XRD patterns (SI, Fig. 1) reveal the fluorite crystalline structure of the different ceria supports with no evidence of platinum diffraction peaks, which suggests an average platinum size <2 nm in agreement with the TEM characterisation. The superior activity of the Pt/CeO_2 nanorods is directly related to the constraints of the 1D (9.1 nm crystallite size and a 7 nm average diameter, Table 1) [21], while the larger crystallite size of the ceria nanocubes makes their re-oxidation by water more difficult [22], reducing its catalytic activity.

The average platinum particle size was estimated by CO pulse chemisorption at room temperature assuming hemispherical metal particles. The average particle size ranges from 0.8 nm in the 1.5 wt.% Pt/CeO_2 particles to 1.0 nm in the 1.5 wt.% Pt/CeO_2 rods and 1.5 nm in the 1.5 wt.% Pt/CeO_2 cubes. It is likely that these metal particle sizes are underestimated due to the potential oxidation of CO to CO_2 using oxygen from the ceria in the presence of platinum. The catalytic activity of the different nanostructured catalysts can be in part due to the variation of the platinum particle size, despite the relatively small differences of mean values (ranging between 0.8 and 1.5 nm). The actual effect of the metal size is still argued in the literature. On one hand, it has been previously shown that the WGS reactivity is independent on platinum sizes < 2 nm [23,24], however, in-depth studies considering the length of periphery between Pt and ceria support clearly demonstrate the particle size–activity relationship [25]. Additionally, such relationships depend on the feed gas composition and reaction temperature.

Similar activation energy values between 45–50 kJ mol^{-1} (Table 1) are shown by all the Pt/CeO_2 catalysts calculated using the Arrhenius' plot (Fig. 1B), where the specific rate values are calculated considering

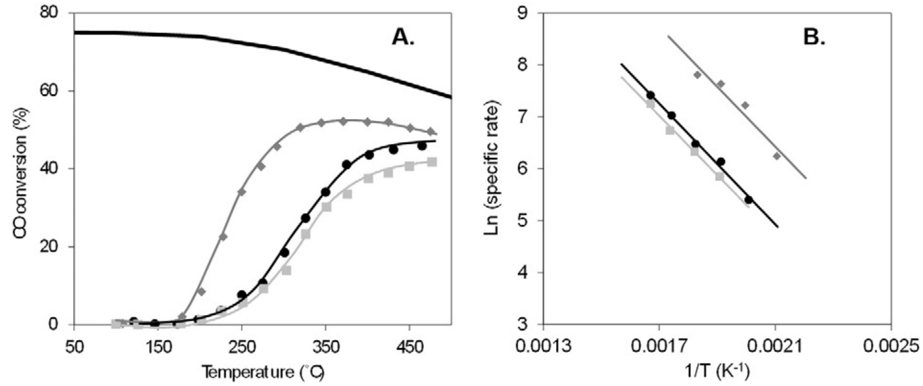

Fig. 1. A. WGS activity of 1.5 wt.% Pt/nanostructured ceria as a function of reaction temperature. B Arrhenius plot where specific rate values are expressed in mol CO converted·mol Pt·h^{-1} ♦ Pt/CeO_2 nanorods ■ Pt/CeO_2 nanocubes ● Pt/CeO_2 nanoparticles. Solid line represents the thermodynamic equilibrium.