Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 112 (2006) 49–52

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of the nature of the support on the catalytic performance of noble metal catalysts for the water–gas shift reaction

Paraskevi Panagiotopoulou, Dimitris I. Kondarides *

Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece

---

Abstract

The catalytic activity of supported noble metal catalysts (Pt, Rh, Ru, and Pd) for the WGS reaction is investigated with respect to the physichochemical properties of the metallic phase and the support. It has been found that, for all metal-support combinations investigated, Pt is much more active than Pd, while Rh and Ru exhibit intermediate activity. The turnover frequency (TOF) of CO conversion does not depend on metal loading, dispersion or crystallite size, but depends strongly on the nature of the metal oxide carrier. In particular, catalytic activity of Pt and Ru catalysts, is 1-2 orders of magnitude higher when supported on "reducible" (TiO_2, CeO_2, La_2O_3, and YSZ) rather than on "irreducible" (Al_2O_3, MgO, and SiO_2) metal oxides. In contrast to what has been found in our previous study over Pt/TiO_2 catalysts, catalytic activity of dispersed Pt does not depend on the structural and morphological characteristics of CeO_2, such as specific surface area or primary crystallite size.

Keywords: Water–gas shift; Noble metal catalysts; Reducible oxides; CeO_2

---

1. Introduction

The interest for the water–gas shift (WGS) reaction has grown significantly during the last few years, as a result of the recent advancements in fuel cell technology and the need for developing fuel processors capable of converting carbonaceous fuels into hydrogen [1,2]. The role of the WGS reactor in such systems is to provide primary CO cleanup and secondary hydrogen production. The maximum CO conversion which can be achieved in a WGS reactor is limited by chemical equilibrium. As a result, it is important to develop stable and selective catalysts with sufficiently high activity at low temperatures which, for typical PEM fuel cell applications, are in the range of 200–280 °C [2].

Conventional WGS catalysts cannot be used in small-to-medium-scale fuel cell systems for power generation, mainly due to restrictions in volume, weight and cost, and also due to problems related to their pyrophoricity and requirement for lengthy precondition steps [3]. The use of supported noble metal catalysts may offer significant advantages, including operation at higher temperatures, where kinetics are more favorable, no need of activation prior to use, no degradation on exposure to air or temperature cycles and availability of conventional wash-coating technologies.

In our previous study [4], the effects of structural and morphological characteristics of the metallic phase and the support on the WGS activity have been investigated over TiO_2-supported noble metal catalysts. It has been found that the turnover frequency does not depend on the structural characteristics of the dispersed metal. However, activity was found to depend strongly on the primary crystallite size of the TiO_2 support [4]. Our investigation is extended in the present study to other noble metal-support combinations, in an attempt to identify the role of the nature and characteristics of the support for the title reaction. The aim is to identify the key physichochemical parameters which mainly determine the WGS activity of supported noble metal catalysts.

2. Experimental

Catalysts were prepared employing the wet impregnation method [4] with the use of $(NH_3)_2Pt(NO_2)_2$, $Ru(NO)(NO_3)_3$, $(NH_3)_2Pd(NO_2)_2$ or $Rh(NO_3)_3$ as metal precursor salts and the following commercial metal oxide powders as supports (in parentheses are given the specific surface areas determined with the BET method): CeO_2 (3.3 m^2/g), TiO_2 (42 m^2/g), yttria-stabilized zirconia (YSZ, 12 m^2/g), Al_2O_3 (83 m^2/g), MgO

---

* Corresponding author. Tel.: +30 2610 969527; fax: +30 2610 991527.
E-mail address: dimi@chemeng.upatras.gr (D.I. Kondarides).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.026

(22 m^2/g), La_2O_3 (7 m^2/g), and SiO_2 (144 m^2/g). The metal loading of the catalysts thus prepared varied between 0.1 and 5 wt.%. Carriers and catalysts were characterized with respect to their specific surface area, exposed metallic surface area and crystallite size employing nitrogen physisorption at the temperature of liquid nitrogen, selective chemisorption of H_2 and/or CO, and X-ray diffraction (XRD) [4].

The effect of the structural and morphological characteristics of the support has been investigated over Pt catalysts (0.5 wt.%) supported on cerium dioxide carriers with variable specific surface area and primary CeO_2 crystallite size. Ceria samples were prepared by an alkoxide method [5] with the use of $Ce(NO_3)_3 \cdot 6H_2O$ as a cerium precursor, diethylamine as a precipitant and ethanol or butanol as diluting agents. Calcination of the resulting powders at temperatures between 450 and 600 °C for 3 h resulted in materials with specific surface areas ranging between 24 and 57 m^2/g, and primary crystallite sizes of CeO_2 (determined by XRD line broadening) ranging between 10 and 21 nm.

The catalytic performance of the prepared samples for the WGS reaction was investigated in the temperature range of 150–550 °C using a feed stream consisting of 3% CO and 10% H_2O (balance He). The mass of catalyst used in these experiments was typically 100 mg (particle size: $0.18 < d < 0.25$ mm) and the total flow rate was 200 cm^3/min. Measurements of intrinsic rates were obtained in separate experiments under differential reaction conditions. Results were used to determine the turnover frequencies (TOFs) of carbon monoxide consumption, defined as moles of CO converted per surface noble metal atom per second. Details of the methods and procedures employed can be found elsewhere [4].

3. Results and discussion

3.1. Influence of the nature of the support on catalytic activity

The effect of the nature of the oxide carrier on the catalytic performance of supported noble metal catalysts has been investigated over platinum catalysts with the same metal loading (0.5 wt.% Pt) supported on a variety of commercial oxide powders. Results of catalytic performance tests (not shown for brevity) showed that, under the experimental conditions employed, the Pt/TiO_2 catalyst is the most active one, exhibiting measurable CO conversions at temperatures as low as 150 °C and reaching equilibrium at 350–400 °C. Platinum catalysts supported on CeO_2, La_2O_3, and YSZ are active at temperatures higher than 200 °C and reach equilibrium conversions at ca 450 °C, while Al_2O_3-supported samples become active at sufficiently higher temperatures. Finally, MgO- and SiO_2-supported platinum catalysts are practically inactive in the temperature range of interest, since temperatures above 450 °C are required in order to achieve conversions of CO higher than 20%.

Results of specific reaction rates measured over the Pt/metal oxide catalysts under differential reaction conditions are summarized in the Arrhenius diagram of Fig. 1A. It is observed that the TOF of CO conversion depends strongly on the nature of the oxide support, with Pt being ca two orders of magnitude more active when supported on TiO_2 than on SiO_2. Titania-supported platinum is clearly the most active catalyst at low temperatures, with its TOF at 200–220 °C being twice as that of Pt/CeO_2 and ca. 30 times higher than that of Pt/Al_2O_3 (Fig. 1A). It is very important to note that platinum catalysts exhibit significantly higher activities when supported on ‘‘reducible’’ (TiO_2, CeO_2, La_2O_3, and YSZ) rather than on ‘‘irreducible’’ oxides (Al_2O_3, MgO, and SiO_2). The apparent activation energies (E_a) of the WGS reaction were calculated from the slopes of the straight lines presented in Fig. 1A. It has been found that E_a varies significantly, depending on the nature of the carrier, ranging from 13.9 kcal/mol over Pt/SiO_2 to 27 kcal/mol over Pt/YSZ catalysts.

Qualitatively similar results obtained from supported Ru catalysts are shown in Fig. 1B. It is observed that, as in the case of Pt, the activity of Ru is significantly improved when supported on reducible (TiO_2, CeO_2, and YSZ) rather than on irreducible (Al_2O_3) oxide supports. Results presented in Fig. 1 are in accordance with the ‘‘regenerative’’ reaction mechanism, which has been proposed for the WGS reaction over conventional mixed oxide catalysts [6] and supported noble metal catalysts [7].

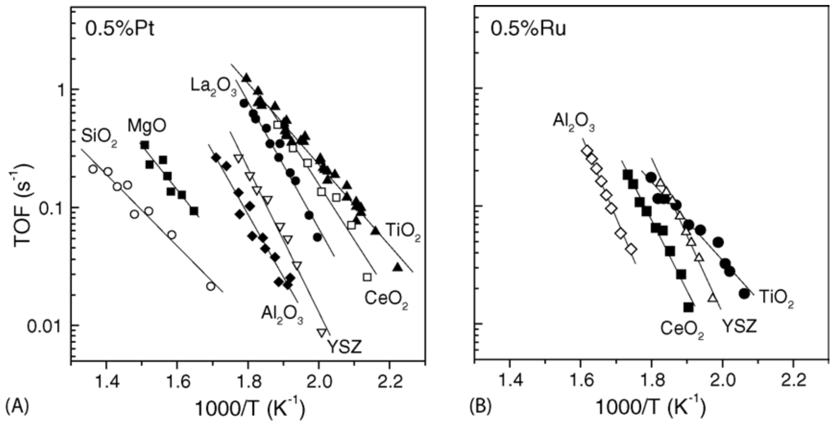

Fig. 1. Effect of the nature of the support on the turnover frequency of CO conversion of (A) Pt and (B) Ru catalysts (0.5 wt.%) supported on the indicated metal oxide powders.

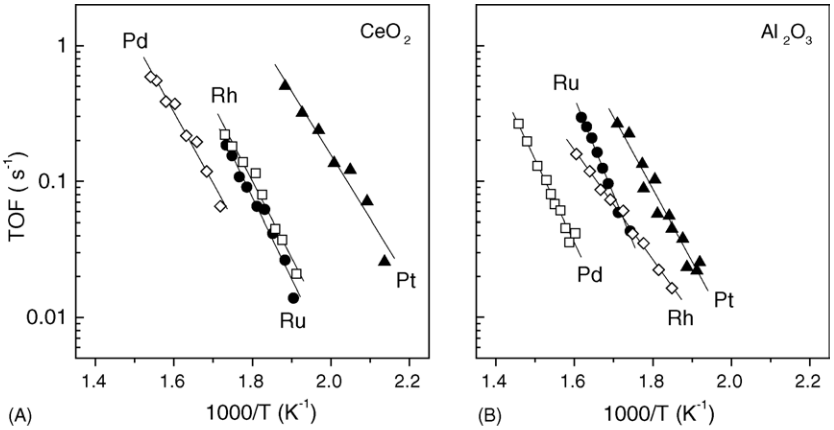

Fig. 2. Arrhenius plots of rates (TOF) of CO conversion obtained from Pt, Rh, Ru, and Pd catalysts (0.5 wt.%) supported on (A) CeO_2 and (B) Al_2O_3.

According to this mechanism, the CO molecules adsorbed on the metal are oxidized by oxygen originating from the support which in turn is oxidized by water [7].

3.2. Effect of the nature of the dispersed metallic phase

The effect of the nature of the metallic phase has been investigated over Pt, Rh, Ru, and Pd catalysts (0.5 wt.%) supported on CeO_2 and Al_2O_3, and results of kinetic measurements are summarized in Fig. 2. It is observed that, for M/CeO_2 catalysts (Fig. 2A), activity follows the order of $Pt > Rh \approx Ru > Pd$, with Pt being 15–20 times more active than Rh and Ru and 50 times more active than Pd, at 250 °C. It is important to note that the apparent activation energy (E_a) of the reaction is practically the same for all CeO_2-supported metals investigated, taking values of ca 24 kcal/mol. Qualitatively similar results were obtained previously for M/TiO_2 catalysts [4], where the same ranking of activity of the metals has been observed. As in the present case, the apparent activation energy has been found to be the same for all TiO_2-supported noble metal catalysts (15.5 kcal/mol). The fact that E_a does not depend on the nature of the metallic phase but only on the nature of the support for M/CeO_2 (Fig. 2) and M/TiO_2 [4] catalysts provides evidence that, for noble metals supported on ‘‘reducible’’ metal oxides, the dominating contribution to the activation energy originates from a reaction step associated with the metal oxide (e.g. water adsorption/activation, surface reaction) [4].

For metals supported on ‘‘irreducible’’ oxide carriers, such as M/Al_2O_3 samples (Fig. 2B), the activity of dispersed metals follows more or less the same order as in the cases of M/CeO_2 (Fig. 2A) and M/TiO_2 [4] catalysts. However, the activation energy of the reaction depends significantly on the nature of the metallic phase, taking values of 24.9 kcal/mol for Pt, 27.9 kcal/mol for Rh, 32.7 kcal/mol for Ru, and 18.4 kcal/mol for Pd. This implies that, under the present experimental conditions, a different reaction step, probably related to the decomposition of surface formates [8], is the rate-limiting one over Pt/Al_2O_3 catalysts.

Results discussed above indicate that reducibility of the oxide support plays a crucial role on the catalytic performance of dispersed noble metal catalysts. Reducibility of the metal oxide carrier may either have a direct effect on activity, as dictated by the redox mechanism [7], or an indirect one, as proposed by Jacobs et al. [9,10]. The latter authors investigated the reaction mechanism over Pt/CeO_2 catalysts and found that reduction of CeO_2 is accompanied by a marked increase in the population of geminal OH groups, which yield formates upon adsorption of CO [9,10]. Decomposition of surface formates is proposed to be the rate-limiting step, in agreement with the early work of Shido and Iwasawa [8].

3.3. Effect of structural and morphological characteristics of catalysts

In our previous study [4], it has been found that catalytic activity of Pt/TiO_2 and Ru/TiO_2 catalysts does not depend on metal loading or crystallite size. In order to check if the same holds for other noble metal/support combinations, two sets of Pt/CeO_2 and Pt/Al_2O_3 catalysts with variable metal loading in the range of 0.1–5.0 wt.% were prepared and tested for their catalytic activity. Results obtained are summarized in the Arrhenius plots of Fig. 3. It is observed that catalytic activity

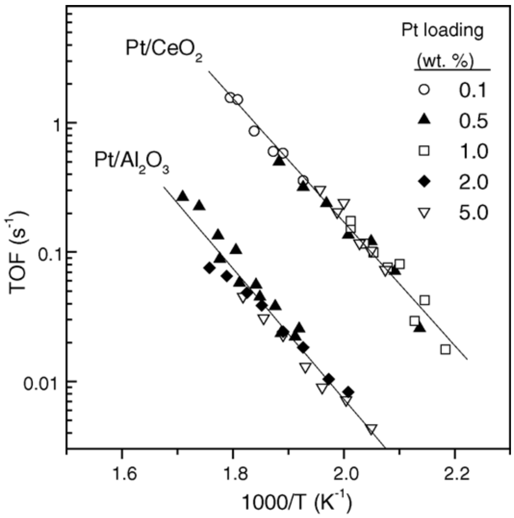

Fig. 3. Effect of metal loading (0.1–5.0 wt.%) on the rate of CO conversion obtained from Pt/CeO_2 and Pt/Al_2O_3 catalysts.

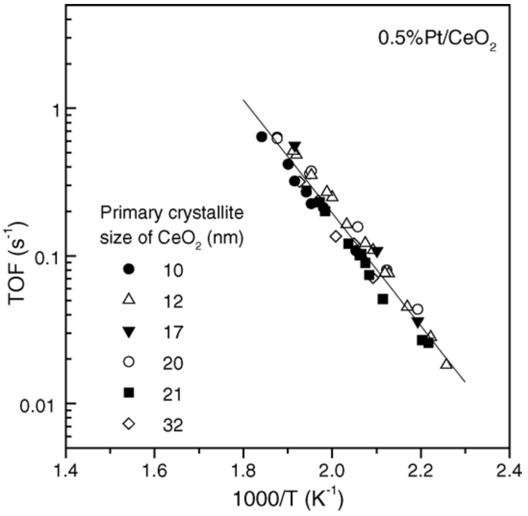

Fig. 4. Arrhenius plot of rates (TOF) of CO conversion obtained from Pt catalysts (0.5 wt.%) supported on CeO_2 carriers of variable specific surface area and primary crystallite size.

does not depend on Pt loading or crystallite size, which varies between 2.0–9.1 nm for Pt/CeO_2 and 0.9–1.7 nm for Pt/Al_2O_3 catalysts. Based on the present (Fig. 3) and previous [4] results obtained from four different metal-support combinations, it may be safely concluded that, as far as the metallic phase is concerned, the reaction is structure-insensitive for both ‘‘reducible’’ and ‘‘irreducible’’ metal oxide carriers.

The effect of structural and morphological properties of ceria on the catalytic performance of supported Pt has been investigated with the use of the self-prepared CeO_2 samples and a commercial CeO_2 powder. Results are summarized in Fig. 4. It is observed that the TOF of CO conversion and the apparent activation energy of the reaction do not depend on the characteristics of the support, at least in the range of surface areas (3.3–57 m^2/g) and primary crystallite sizes (10–32 nm) investigated. Completely different results were obtained previously from Pt/TiO_2 catalysts [4], where the TOF was found to increase by more than two orders of magnitude with decreasing the primary crystallite size of TiO_2 from 35 to 16 nm, with a parallel decrease of activation energy from 16.9 to 11.9 kcal/mol. The difference between the TiO_2- and the CeO_2-supported catalysts may be due to the fact that CeO_2 is characterized by high reducibility, the change of which by decreasing its crystallite size does not have a significant effect on catalytic activity, at least under the experimental conditions employed.

4. Conclusions

The catalytic performance of supported noble metals for the WGS reaction depends strongly on the nature of both the metallic phase and the metal oxide support. Platinum catalysts are generally more active than Ru, Rh, and Pd, and exhibit significantly higher activity when supported on ‘‘reducible’’ rather than on ‘‘irreducible’’ oxides. Titania-supported platinum is more active than the well-studied Pt/CeO_2 catalyst, especially in the temperature range of 200–250 °C. When noble metals are dispersed on ‘‘reducible’’ oxides, such as CeO_2 and TiO_2, the apparent activation energy of the reaction does not depend on the nature of the metallic phase but only on the nature of the support. In contrast, E_a differs from one metal to another when supported on an irreducible oxide, such as Al_2O_3, indicating that a different reaction mechanism is operable. The specific reaction rate (TOF) does not depend on metal loading, dispersion or crystallite size for all metal-support combinations investigated. Finally, activity of Pt/CeO_2 does not depend on the structural and morphological characteristics of the support, in contrast to what has been found previously for Pt/TiO_2 catalysts.

Acknowledgements

This work is funded by the General Secretariat of Research and Technology (GSRT) Hellas and the Commission of the European Community, under the PENED 2001 Programm (contract 01ED561).

References

[1] D.L. Trimm, Z.I. Önsan, Catal. Rev. 43 (2001) 31.
[2] A.F. Ghenciu, Curr. Opin. Solid State Mater. Sci. 6 (2002) 389.
[3] J.M. Zalc, D.G. Löffler, J. Power Sources 111 (2002) 58.
[4] P. Panagiotopoulou, D.I. Kondarides, J. Catal. 225 (2004) 327.
[5] J.-G. Li, T. Ikegami, J.-H. Lee, T. Mori, Acta Mater. 49 (2001) 419.
[6] D.S. Newsome, Catal. Rev. Sci. Eng. 21 (1980) 275.
[7] X. Wang, R.J. Gorte, J.P. Wagner, J. Catal. 212 (2002) 225.
[8] T. Shido, Y. Iwasawa, J. Catal. 141 (1993) 71.
[9] G. Jacobs, E. Chenu, P.M. Patterson, L. Williams, D. Sparks, G. Thomas, B.H. Davis, Appl. Catal. A 258 (2004) 203.
[10] G. Jacobs, P.M. Patterson, U.M. Graham, D.E. Sparks, B.H. Davis, Appl. Catal. A 269 (2004) 63.