



Effect of the support on the catalytic stability of Rh formulations for the water–gas shift reaction

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ABSTRACT

The stability of Rh(0.6)/La₂O₃ and Rh(0.6)/La₂O₃(27)·SiO₂ catalysts used in the water–gas shift reaction (WGS) was studied. In order to understand the different behavior of the two formulations, XRD, Raman spectroscopy and operando-DRIFTS were employed. It was demonstrated that Rh/La₂O₃·SiO₂ showed a constant activity after 50 h on stream and that it was made up of La₂Si₂O₇ with very low crystallinity and SiO₂. On the other hand, Rh/La₂O₃ after use evolved to a mixture of oxycarbonates and lanthanum hydroxide evidenced by XRD and confirmed by Raman spectroscopy. This solid suffered a significant deactivation which was assigned to the formation of very small amounts of formate and carbonate residues. These residues disappeared after being burnt in air at 673 K and the initial catalytic activity was restored. The results obtained were useful to explain the reasons for the different stability of the two formulations and could have implications for the design of active catalysts used in the WGS and in the processes in which it is involved.

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1. Introduction

The water–gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, is an important step in several industrial processes [1,2]. It is used to increase hydrogen production and remove CO before ammonia synthesis in refinery hydroprocesses, or to adjust the H₂/CO molar ratio in methanol production and Fischer–Tropsch synthesis.

The WGS reaction is one of the key steps in a typical fuel processor (FP) used in CO-free hydrogen production. The WGS reaction unit in a FP follows the reformer and reduces the CO concentration while increasing the hydrogen yield. Since the reversible WGS reaction is moderately exothermic and equilibrium-limited, lower CO levels can be achieved at low temperatures. Nevertheless, high temperatures are required to increase the reaction rate. In a FP, the WGS reaction is normally performed in two serial reactors, namely the high-temperature shift reactor operating at 623–773 K, and the low-temperature shift reactor operating at 453–513 K for obtaining high activity and conversion simultaneously [3]. In order to obtain H₂ containing <10 ppm CO for use in PEM fuel cells, a second purification step is needed (COPrOx or PSA).

An attractive alternative is to conduct the WGS reaction in a membrane reactor. In this way, only one vessel is needed and the CO conversion increases above equilibrium value leaving behind a stream rich in CO₂ ready for sequestration. The catalyst needed to achieve this goal should operate at ca. 670 K to strike a balance between the negative effect of CO upon H₂ permeability [4] and the palladium membrane durability. Both factors decrease with temperature.

To optimize the reactor operation, a high-temperature, active, stable catalyst is required. The new formulation should not form carbonaceous residues because carbon has a great Pd affinity which rapidly destroys the membrane.

Several commercial formulations are available to conduct the reaction at low or high temperature [5]. There has been great interest in the development of active, selective, thermally stable, poison-resistant, non-pyrophoric noble-metal based WGS reaction catalyst formulations supported on metal oxide carriers. They exhibit much faster high-temperature kinetics compared to conventional ones and offer other significant advantages such as no need of activation prior to use, no degradation on exposure to air or temperature cycles, which could result in the reduction of reactor size and other costs. Note that in FP, the WGS reactors using commercial HT catalysts are the largest ones [6]. This is another factor that stimulates the search for more active catalysts. Among the noble metals, Pt and Rh are the best candidates. Rh has been

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