Mechanism analysis of the water gas shift reaction over supported Pt catalysts

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Introduction
Hydrogen demand is expected to increase in the future due to its use in fuel cells and WGS reaction is an important step in maximizing hydrogen generation. The water gas shift (WGS) is a reversible, exothermic reaction (CO + H₂O ↔ CO₂ + H₂, ΔH = -41.1 KJ/mol). In the literature, two main mechanisms for WGS reaction have been proposed, the redox mechanism and the associative formate route. The first mechanism implies a successive oxidation by adsorbed oxygen from H₂O and reduction of the active site by CO as CO is oxidized to CO₂. In the second mechanism, dissociates adsorbed hydroxyl group from the support combines with CO to form formates which eventually decomposes into CO₂ and H₂. One possibility for hydroxyl groups is the dissociation of H₂O at support oxygen vacancies during the reduction process [1]. Another possibility is direct formation of these groups via H₂ dissociation on the metal and spillover to the oxide [2]. The aim of this work is to analyze the effect of the support in Pt catalysts using DRIFTS. SiO₂, CeO₂ and TiO₂ were used as supports.

Experimental
Pt (0.34-0.5%) supported catalysts were prepared by incipient wetness impregnation of SiO₂ (Grace Davison), CeO₂ (prepared according to [3]), TiO₂-LS (Degussa P-25) and TiO₂-HS (Hombifine N) with aqueous solution of [Pt(NH₃)₄(NO₃)₂]. Samples were characterized by BET surface area, XRD, H₂ chemisorption. The activity of the catalysts were studied using conversion vs. time tests at 250°C. The reaction was also followed by DRIFTS at different temperatures from 30°C to 300°C.

Results and discussion
Specific surface area values (Table 1) show that the impregnation did not modify the structure of the supports. Moreover, no platinum phase was detected in the X-ray diffractograms probably due to its low amount in the solids.
WGS was also carried out on platinum catalysts by performing X vs time tests at 250°C. The reaction rates (\(r_{CO}^0\), mol CO/g Pt.h) and turnover frequencies (TOF, h⁻¹) of CO conversion were calculated from the X_CO vs time tests. As shown in Table 1, the activity of platinum catalysts varies as follows: TiO₂-AS>>TiO₂-BS>CeO₂>>SiO₂.
The chemical species formed on Pt/CeO$_2$ and Pt/TiO$_2$ during the WGS reaction were identified by DRIFT (Figure 1). Results showed that the reaction occurs via the interaction between CO and hydroxyl groups of the support, with formation of formate intermediates. The intensity of formate (2900-2700 cm$^{-1}$) bands was lower on Pt/TiO$_2$ catalysts than on Pt/CeO$_2$. The lower stability of formate intermediates on Pt/TiO$_2$ would explain the higher activity displayed by these catalysts. Furthermore, the higher activity of Pt/TiO$_2$-HS compared to Pt/TiO$_2$-LS could be attributed to a higher amount of hydroxyl groups in the former due to its higher specific surface area. No formate bands were detected on Pt/SiO$_2$, thereby suggesting that the WGS reaction on this catalyst occurs via a redox mechanism.

Conclusions
The reducibility of the support highly influences on catalytic activity of Pt catalysts in WGS reaction and the mechanism of the reaction. DRIFTS results would suggest that in the case of Pt/SiO$_2$ the reaction occurs via a redox mechanism. In contrast, for catalysts whose supports are reducible oxides (TiO$_2$-AS, TiO$_2$-BS, CeO$_2$) formate intermediates were observed. These species are less stable on Pt/TiO$_2$ than on Pt/CeO$_2$ which would explain its better activity.

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References