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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 ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, $\Delta H = -41,1$ 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 H_2O and reduction of the active site by CO as CO is oxidized to CO_2 . In the second mechanism, dissociates adsorbed hydroxyl group from the support combines with CO to form formates which eventually decomposes into CO_2 and H_2 . One possibility for hydroxyl groups is the dissociation of H_2O at support oxygen vacancies during the reduction process [1]. Another possibility is direct formation of these groups via H_2 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. SiO_2 , CeO_2 and TiO_2 were used as supports.

Experimental

Pt (0.34-0.5%) supported catalysts were prepared by incipient wetness impregnation of SiO_2 (Grace Davison), CeO_2 (prepared according to [3]), TiO_2 -LS (Degussa P-25) and TiO_2 -HS (Hombifine N) with aqueous solution of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$. Samples were characterized by BET surface area, XRD, H_2 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: $\text{TiO}_2\text{-AS} \gg \text{TiO}_2\text{-BS} > \text{CeO}_2 \gg \text{SiO}_2$.

The chemical species formed on Pt/CeO₂ and Pt/TiO₂ 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/TiO₂ catalysts than on Pt/CeO₂. The lower stability of formate intermediates on Pt/TiO₂ would explain the higher activity displayed by these catalysts.

Table 1. Characteristics and catalytic activity of samples.

Catalyst	Sg (m ² /g)		D (%)	r _{CO} ⁰ (mol CO g _{Pt} ⁻¹ h ⁻¹)	TOF (h ⁻¹)
	Supports	Catalysts			
Pt/SiO ₂	230	253	52	0,292	110
Pt/CeO ₂	54	41	37	2,750	1450
Pt/TiO ₂ -LS	54	56	13	3,653	5480
Pt/TiO ₂ -HS	186	172	11	5,850	10370

Furthermore, the higher activity of Pt/TiO₂-HS compared to Pt/TiO₂-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/SiO₂, thereby suggesting that the WGS reaction on this catalyst occurs via a redox mechanism.

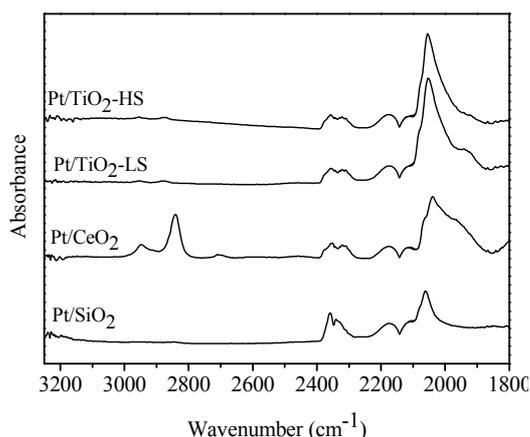


Figure 1. DRIFTS spectra of WGS reaction at 250°C, 3%CO/10%H₂O/N₂.

Pt/SiO₂ the reaction occurs via a redox mechanism. In contrast, for catalysts whose supports are reducible oxides (TiO₂-AS, TiO₂-BS, CeO₂) formate intermediates were observed. These species are less stable on Pt/TiO₂ than on Pt/CeO₂ which would explain its better activity.

Acknowledgements

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References

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