

Mechanistic insights into r-WGS reaction on Rh and Pt via a combined experimental and structure-dependent microkinetic analysis

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Highlights

- The oxygen affinity of the catalyst determines the Reverse Water-Gas Shift reaction mechanism.
- CO₂ is activated *via* dissociation route on Rh and *via* a H-mediated pathway on Pt.
- Theoretical structure-dependent analysis is pivotal for a detailed description of reaction mechanisms.

1. Introduction

In the last few decades, there has been a significant increase in atmospheric CO₂ concentration, with carbon dioxide being the primarily responsible gas for the greenhouse effect. In this context, the upgrading of CO₂ produced by hard-to-replace processes into more valuable products is a compelling solution to cut the net CO₂ emissions. The Reverse Water-Gas Shift (r-WGS) reaction stands out as a promising approach, generating CO as a crucial building block for the chemical industry. Despite its importance, there are still a lot of debates concerning the precise mechanism of this reaction, therefore a thorough mechanistic analysis is fundamental for the effective catalyst optimization [1,2]. As demonstrated by previous theoretical investigations from our group, the activation of CO₂ depends on the oxyphilic nature of the catalyst material [3]. In this study, we combine both theoretical and experimental methodologies to shed light on the r-WGS reaction's elementary steps. More in detail, we investigate how the reaction mechanism changes according to the specific oxygen-affinity of the surface, employing two different catalyst materials, 4wt.% Rh/ α -Al₂O₃ and 4wt.% Pt/ α -Al₂O₃. On one side, the experiments make it possible to identify the nature of the kinetically relevant transition state for the specific material. On the other side, the structure-dependent microkinetic analysis was pivotal to unveil the identity of the active site in terms of atomistic configuration, providing fundamental insights into the reaction mechanism.

2. Methods

Non-commercial 4wt.% Rh/ α -Al₂O₃ and 4wt.% Pt/ α -Al₂O₃ were prepared and tested in this work. The α -Al₂O₃ support was obtained from commercially available γ -Al₂O₃, through calcination at 1200°C. The preparation of the catalytic powder was made with the incipient wetness impregnation of the support, with Rh(NO₃)₃ and Pt(NO₃)₄ solutions. The catalytic tests were performed in powder and annular reactors (60mg of diluted (1:20) catalyst, to ensure an isothermal bed). PBE-D3 calculations were performed using QuantumEspresso. The morphology of heterogeneous catalyst nanoparticles as a function of the gas chemical potential is determined by means of *ab initio* thermodynamics and Wulff construction method. On the different facets, the occurrence of 23 elementary steps is investigated to describe the r-WGS reaction mechanism. The climbing-image nudged elastic (CI-NEB) is adopted for the evaluation of the geometry of the transition states for each elementary step.

3. Results and discussion

We carried out a comprehensive experimental investigation of the kinetic mechanism governing the r-WGS reaction considering a wide range of operating conditions. The reaction rate of the r-WGS reaction measurements exhibited a direct proportionality on the concentrations of CO₂ for both catalysts. On the contrary, the dependence on H₂ concentration changed between Rh and Pt and was also affected by the specific operating conditions. On rhodium-based catalyst, the rate was found to depend on H₂ only at low concentrations, transitioning to a 0th-order dependence as H₂ concentration increased. Conversely, the reaction rate showed a dependency on H₂ on Pt in the entire range of operating conditions. In addition

to that, CO caused a mild inhibition effect on both catalysts at 600°C. Pt and Rh possess differing affinities for oxygen (the binding energies are -4.5 and -5.3 eV respectively). As suggested in [3], oxophilic surfaces tend to activate CO₂ via dissociation into CO* and O*, while surfaces with a lower oxophilicity are more likely to facilitate a hydrogen-mediated pathway. This experimental evidence was therefore rationalized by proposing that on Rh-based catalyst, CO₂ is activated through dissociation into CO* and O* without direct involvement of H₂, while on Pt-based catalyst, CO₂ activation occurs *via* a hydrogen-mediated route with the formation of a COOH* intermediate. To elucidate this mechanistic interpretation, we conducted a structure-dependent microkinetic analysis on both materials based on DFT calculations [4]. We accounted for the presence of several facets that the catalyst nanoparticles can expose under reaction conditions, considering both their activity and abundance with respect to the total catalyst surface. This structure-dependency inclusion is fundamental for the identification of the dominant active site that determines the kinetics of the macroscopic reaction. As shown in Fig.1, CO₂ is found to be activated *via* dissociation into CO* and O* on Rh and *via* a hydrogen-mediated route on Pt, in agreement with experiments. In the case of rhodium, we found that Rh(100) is the dominant active site, since its relatively low abundance is counterbalanced by its high turnover frequency. In the case of platinum, Pt(111) and Pt(211) are the most abundant facets of Pt nanoparticles. However, the activity of Pt(211) is inhibited by the competitive adsorption of CO*. Thus, Pt(111) is the prevalent active site, producing over than 63% of CO. The degree of rate control (DRC) analysis revealed that, on Rh, CO₂ dissociation is the most kinetically relevant step, while H₂O* formation presents a small but not negligible DRC. The overall reaction rate is indeed proportional to the partial pressure of CO₂, while the mild positive order of H₂ is attributed to the direct proportionality of H₂O* formation. In contrast, on Pt, the rate-determining step is the CO₂* reaction with H* to form t-COOH*. These findings led to apparent reaction orders which fully reconcile with experimental data.

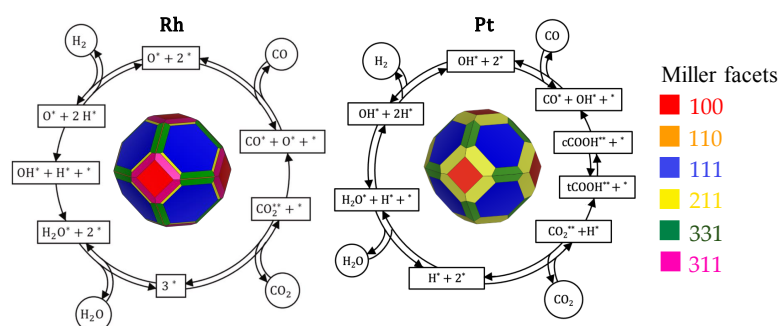


Figure 1. Reaction mechanisms for r-WGS on Rh (left) and Pt (right)

4. Conclusions

In this study we employed a combined theoretical and experimental approach to unveil the r-WGS reaction mechanism, crucial for reducing CO₂ emissions. Using 4wt.% Rh/ α -Al₂O₃ and 4wt.% Pt/ α -Al₂O₃ catalysts, we explored the impact of varying oxygen-affinity on the reaction mechanism. Rh catalyst activates CO₂ through dissociation into CO* and O*, while on Pt the reaction follows a hydrogen-mediated route forming a COOH* intermediate. The structure-dependent methodology adopted for the description of catalyst nanoparticles was essential for the interpretation of experimental measurements. Indeed, it allowed for the identification of the most kinetically relevant steps and of the dominant active sites. These findings make it possible to derive fundamental rate equations for catalyst design and optimization. Project funded under PNRR-NextGenerationEU “Network 4 Energy Sustainable Transition – NEST”.

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Keywords

Active sites; multiscale modeling; density functional theory; reverse water-gas shift.