

Microkinetics of the water-gas shift reaction over Pt and Au supported dual-site catalysts

Olivier Thinon¹, Yves Schuurman^{1*}, Fabrice Diehl², Priscilla Avenier²

¹Institut de Recherche sur la Catalyse et l'Environnement de Lyon, Université Lyon 1, Villeurbanne, 69626, (France)

²IFP-Lyon, Solaize, 69360 (France)

*yves.schuurman@ircelyon.univ-lyon1.fr

Introduction

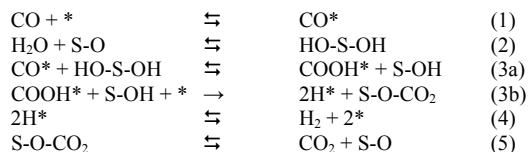
The water gas shift reaction (WGSR) has attracted a renewed interest in the recent past because of its potential application to the CO removal from H₂-rich feed gases for fuel cells. Several mechanisms are proposed in the literature [1, 2] but, until now, no quantitative model taking into account both the metal and the support has been presented. In our study, we propose a microkinetic model based on a dual-site mechanism that describes the WGSR over Pt and Au supported on two different reducible oxides.

Materials and Methods

Pt- and Au-supported catalysts were prepared by incipient wetness impregnation and deposition-precipitation respectively, with the use of (NH₄)₂Pt(NO₃)₆ and HAuCl₄ as metal precursors and the following supports: CeO₂ (~110 m²/g, Rhodia) and TiO₂ (~80 m²/g, Engelhardt). The catalysts have been characterized using techniques such XRD, XPS, TEM. The kinetic study was conducted at ambient pressure, in the temperature range of 150-400°C in a fixed bed reactor with 0.2 g of catalyst, and varying the gas composition over the range 1-20% CO, 1-20% CO₂, 5-25% H₂O and 5-40% H₂, giving ~150 experiments per catalyst.

Results and Discussion

Initial power law rate model yielded the apparent activation energies of catalysts and showed that CO and H₂ adsorb stronger on Pt than on Au. CO₂ has an inhibiting effect on the rate over ceria-supported catalysts. These observations are in good agreement with a dual-site mechanism initially proposed over Pt supported catalysts [3]:



In this mechanism both CO and H₂ chemisorb on the metal whereas CO₂ and H₂O are adsorbed on the support. The reaction between "CO-derived" and "H₂O-derived" adsorbed species takes place at the metal support interface (step 3a and 3b). In order to verify if this model can be widely applied to dual-site WGS catalysts it was assumed that the sorption steps on the metal and support are independent. Consistent and physically correct sorption parameters are required for the 4 samples. The corresponding rate is calculated by numerically integrating the

balances for both the gas and surface species. The data corresponding to all four catalysts were regressed simultaneously with the same sorption parameters for both the reactants and products on the two metals and the two supports (Table 1). Both CO and H₂ adsorb stronger on Pt than on Au. Both CO₂ and H₂O adsorb stronger on CeO₂ than on TiO₂. The microkinetic model describes the data adequately over all 4 samples thus capturing the wide variation in observed reaction orders (figure 1).

Additional evidence for this mechanism comes from TPD (Temperature Programmed Desorption) and transient sorption experiments of CO₂ and H₂O over both the catalysts and the supports. The presence of the metal phase does not change the TPD spectra significantly and confirms the role of the support and the above assumption of independence of the sorption processes. Figure 2 compares the TPD curves simulated on the basis of the above reaction sequence and the parameters from Table 1 for CO₂ and H₂O sorption on ceria. Although the reaction between the adsorbed species has to be further detailed, a consistent set of sorption parameters supports a universal mechanism for dual-site WGS catalysts.

Table 1. Estimated kinetic parameters

Sample	ΔH_{ads} (kJ/mol)				E_a (3) (kJ/mol)
	CO	H ₂	H ₂ O	CO ₂	
Pt/TiO ₂	96	65	48	5	101
Au/TiO ₂	32	33	48	5	82
Pt/CeO ₂	96	65	47	68	128
Au/CeO ₂	32	33	47	68	89

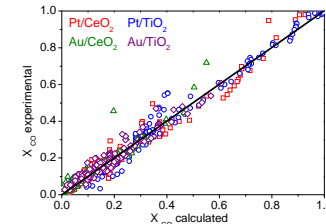


Figure 1: Parity plot

Conclusion

A universal reaction mechanism based on a single route and taking explicitly the different functions (metal, support) into account can describe the WGSR over different catalysts. This approach will allow a more rational design of improved dual-site WGS catalysts.

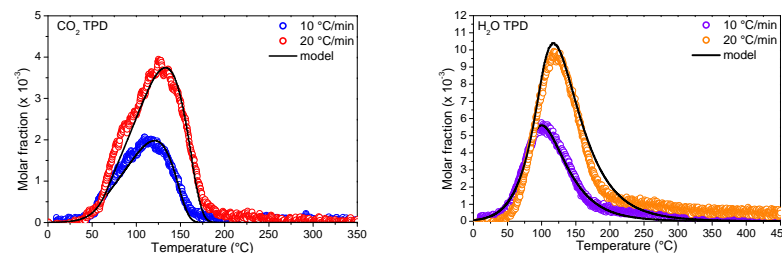


Figure 2. Temperature Programmed Desorption of CO₂ and H₂O over Pt/CeO₂ catalysts.

References

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