

***In-Situ* ATR-IR study of CO oxidation over Pt/Al₂O₃ and Pd/Al₂O₃ in water - promotion effects by water and pH**

B.L. Mojet*, S.D. Ebbesen, L. Lefferts

Catalytic Processes and Materials, Faculty of Science and Technology, MESA+, University of Twente, P.O. box 217, 7500 AE, Enschede, The Netherlands,

*B.L.Mojet@utwente.nl

Introduction

The chemical industry is continuously searching for more cost- and performance-efficient processes, and the trend is therefore to use water as solvent. The selection of water as a solvent offers many benefits: low cost, environmentally friendly, availability, and safety. So far, detailed mechanistic studies of heterogeneous catalytic reactions in water are lacking because it is difficult to study heterogeneous catalysts *in-situ* if the reaction is carried out in water. For gas phase reactions, vibrational spectroscopy is a versatile tool to study adsorption and reaction on catalytic surfaces. However, in liquid phase reactions application of normal transmission infrared spectroscopy is not suitable because water is a very strong absorber of infrared radiation. Attenuated Total Reflection Infrared Spectroscopy (ATR-IR), however, is ideally suited for studying molecular vibrations at the solid-liquid interface because the evanescent wave is restricted to the region near the interface, thereby minimizing the contribution from water.

To explore this new field of characterizing supported noble metal catalysts in water, we studied the adsorption and oxidation of CO, as a function of pH, in water on Pt/Al₂O₃ and Pd/Al₂O₃ using *in-situ* ATR spectroscopy,

Materials and Methods

Each catalyst film was prepared on an ZnSe internal reflection element (IRE) by evaporating the appropriate catalyst suspension as extensively described elsewhere[1]. Subsequently the catalyst film/IRE was calcined and reduced resulting in a smooth and stable catalyst layer consisting of small particles of a few nanometer size, with a total layer thickness of around 3.5 μm . ATR-IR spectra were recorded with a Tensor FTIR spectrometer (Bruker) at room temperature using a home built stainless steel flow through cell.

Results and Discussion

Comparison of the adsorption of CO from gas phase or water revealed clear spectral differences. If changing from gas phase to water, a significant red shift for adsorbed CO was found. On Pd/Al₂O₃ linear CO shifted from 2091 to 2034 cm^{-1} (57 cm^{-1}), bridged adsorbed CO shifted from 2978 to 2011 cm^{-1} (67 cm^{-1}) and multi bonded CO shifted from 1934 to 1870 cm^{-1} (64 cm^{-1}). Similar shifts were found for Pt/Al₂O₃. Figure 1a shows the peak position of linear CO on Pd/Al₂O₃ as a function of pH. The linear CO peak position shifted from 2045 to 2032 cm^{-1} with increasing pH from 5 to 9. Clearly, from Figure 1 it can be seen that pH affects the observed stretch frequency of adsorbed CO on supported Pd particles. Similar to observations in gas phase with altering support acidity, these shifts indicate a change in the electron density distribution in the metal and/or CO molecule [2,3].

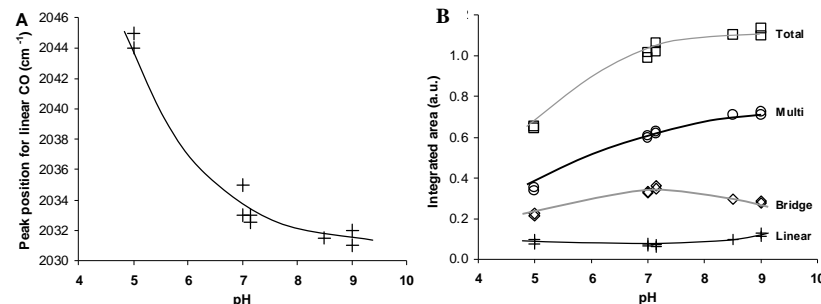


Figure 1. A: ATR-IR frequency of linearly bonded CO on Pd/Al₂O₃ as a function of pH; B: Integrated peak areas of multi bonded, bridge bonded and linear bonded adsorbed CO on Pd/Al₂O₃ as well as the total sum, as a function of pH.

After saturation of the metal surface with CO, water saturated with O₂ was flown over the catalyst to oxidize adsorbed CO. During oxidation of pre-adsorbed CO all peaks for linear and bridged adsorbed CO decreased. Interestingly, the initial oxidation rate in water was twice the oxidation rate in gas phase. Moreover, a linear relation was found between the CO peak position and the initial CO oxidation rate for Pt/Al₂O₃ in liquid phase. On Pd/Al₂O₃ on the other hand, during CO oxidation a clear blue shift in CO stretch frequency of adsorbed CO was observed. The blue shift is attributed to surface oxidation of the supported palladium particles partly covered with CO, indicating that oxidation of palladium is facilitated in water and that surface oxidation of the supported palladium particles occurs easier than surface oxidation of the supported platinum particles. The observations point to an important role of both water and pH in the oxidation of pre-adsorbed CO, which will be discussed in more detail.

Significance

Clearly, ATR-IR spectroscopy holds promise to characterize supported noble metal catalysts in liquid phase reactions. More importantly, this study shows the parallels between support acidity in gas phase reactions and changing pH in liquid phase reactions illustrated by changes in CO peak positions and oxidation rates as a function of catalyst.

Acknowledgments

This work was financially supported by DSM Research The Netherlands.

References

1. Ebbesen S.D.; Mojet, B.L.; Lefferts, L. *J. Catal* 256, 15 (2008).
2. Mojet, B. L.; Miller, J. T.; Ramaker, D. E.; Koningsberger, D. C.*J.Catal* 186, 373 (1999) and references therein.
3. Visser, T; Nijhuis, T.A.; van der Eerden, .A.M.J et al., *J.Phys.Chem.B* 109, 3822 (2005).