HFEPR Studies of ReO_x/Al_2O_3 Olefin Metathesis Catalysts

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Introduction

Olefin metathesis is expected to meet a substantial part of the worldwide olefin shortage. ReO_x/Al_2O_3 catalysts are favorable at certain industrial settings due to their ability to catalyze the reaction at near ambient conditions. Despite decades of research, the nature of ReOx species during the reaction is not well understood due to lack of modern characterization techniques in the past.

Experimental

15.6%ReO_x/Al_2O_3 and 10%ReO_x/10%TaO_x/Al_2O_3 (tantalum promoted) catalysts were pretreated with propylene at 573 K after 773 K dehydration in O_2/He. The HFEPR spectra were recorded on the homodyne spectrometer and its associated 15/17 T superconducting magnet, at 7 K.

Results and Discussion

A typical HFEPR spectrum of 15.6%ReO_x/Al_2O_3 catalyst after 573 K propylene exposure is shown in Fig. 1. The effect of TaO_x does not change the nature of reduced species (results not shown for brevity) since the 10%ReO_x/10%TaO_x/Al_2O_3 catalyst produced the same spectrum. The HFEPR results indicate the presence of Re^{+6} species after propylene treatment. This particular resonance is assigned to Re^{+6} because it originates from a low spin (S = 1/2) state (one unpaired electron) and its g-value (1.75) is well below g = 2, which is expected for less than half-occupied d orbital, and typical for rhenium in general. Mn^{2+} species are also detected due to the impurities in the catalyst support [1].

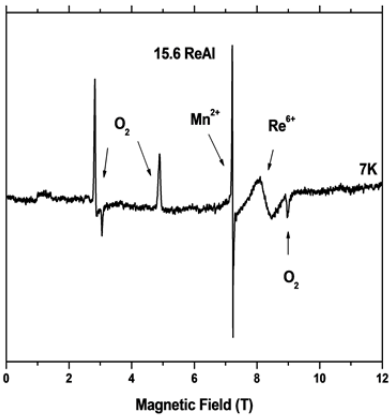

Fig. 1. A 203.2 GHz EPR spectrum of the 15.6%ReO_x/Al_2O_3 catalyst at 7 K after 573 K propylene exposure.

Conclusions

This is the first HFEPR study of ReO_x/Al_2O_3 catalysts. Complemented with other techniques (*in situ* Raman, UV Vis, IR and XAS and kinetics experiments), these results will provide a wealth of information about the nature of catalytically active species and reaction intermediates.

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References

[1] Wertz, J.E., Bolton, J.R., Electron Spin Resonance, **1986**, Chapman, New York.